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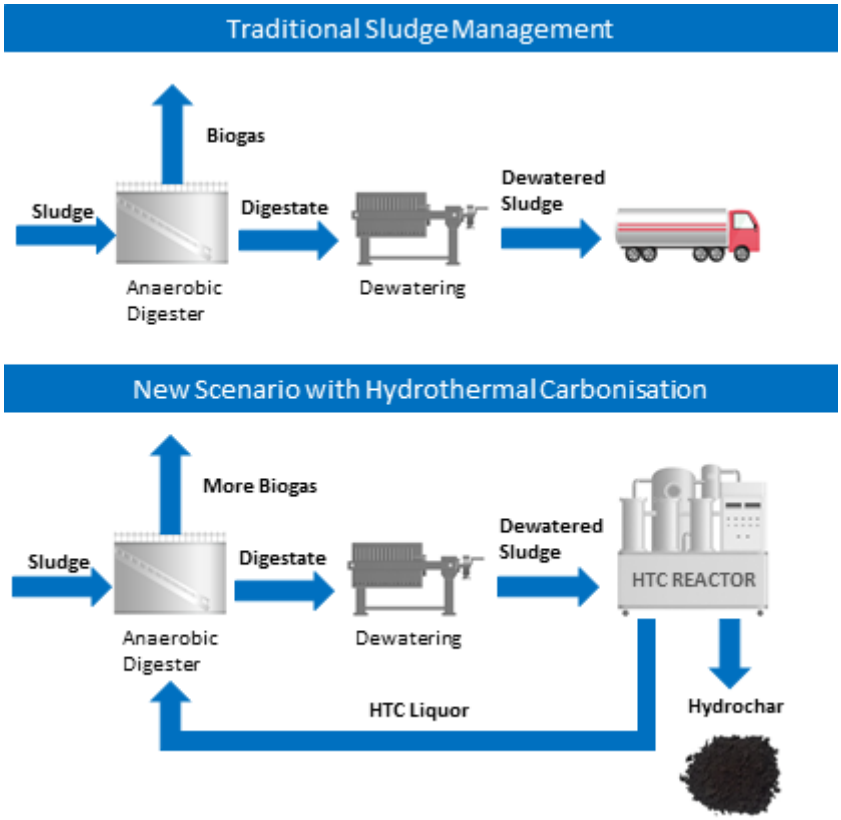
Hydrothermal Processes Applied to Sludge Reduction



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UNIVERSITY OF TRENTO - Italy
Department of Civil, Environmental and Mechanical Engineering

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HYDROTHERMAL PROCESSES APPLIED TO SLUDGE REDUCTION

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Abstract

Conventional Activated Sludge (CAS) systems have been widely implemented to treat wastewater. CAS systems produce huge amounts of waste sludge and its subsequent treatment represents up to 65 % of the operational costs of Waste Water Treatment Plants. The final disposal of sludge is usually performed by landfilling or incineration, involving severe environmental issues. In order to reduce sludge amount, many studies have been conducted, developing new technologies. One of these technologies is HydroThermal Carbonisation (HTC), where sludge is heated up to 180-250 ℃ at water vapour pressure producing a solid product enriched in carbon for different possible exploitations. The aim of this work is to apply HTC to different kinds of sludge such as thickened sludge, digested sludge and dewatered sludge and compare the behaviour of the solid and liquid phases produced by the process. For the purpose, experimental tests were performed at different operating conditions in a lab batch reactor capable to withstand high pressure (140 bar) and temperature (300 ℃). In order to compare the HTC products of the different kinds of sludge, the hydrochars from HTC at different operative conditions were characterized in order to explore possible application of hydrochar and HTC process water.

Keywords: sludge, hydrothermal carbonisation, hydrochar, wastewater treatment plant

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Chapter 0

Research Object and Thesis outline

This Chapter gives the aim and the relevance of the study, providing also the thesis structure.

0.1 Research Object

The first objective was to design, construct and test a Hydrothermal Carbonisation reactor for research purposes that can be used to assess the suitability of the Hydrothermal Carbonisation technology. In order to treat sewage sludge and other waste biomass. The Hydrothermal Carbonisation reactor was designed in accordance with standard technical requirements for vessel under internal pressure in order to ensure proper functionality and safe operation, and it was equipped with a power meter for electrical consumptions in order to evaluate heat of reaction of Hydrothermal Carbonisation process. The second aim was to study the products of Hydrothermal Carbonisation of sewage sludge, namely hydrochar and the Hydrothermal Carbonisation liquor, in order to characterize and valorise them through circular economy concept involving the formation of products from waste, namely sewage sludge, which nowadays is produced in huge amounts.

0.2 Thesis Outline

There are a total of seven chapters which make up this Thesis: chapter 0 (this chapter), provides the aims and the structure of the thesis. Chapter 1 is a literature review of Hydrothermal Carbonisation process, summarising the chemistry and the main operative parameters. The chapter provides an in deep analysis of Hydrothermal Carbonisation of sewage

sludge, highlighting the produced hydrochar applications, characteristics and energy balance. Chapter 2 is a literature review of the anaerobic biodegradability of Hydrothermal Carbonisation process wastewater produced from the application of Hydrothermal Carbonisation of sewage sludge and other kind of feedstock. The chapter provides an assessment of energy balance and main operative parameters that affects anaerobic digestion of hydrothermal carbonisation process wastewater. Chapter 3 is a description of the reactor I designed during my PhD in order to study Hydrothermal Carbonisation process and its heat of reaction; some preliminary results were presented in IconBM conference (Bologna, Italy, 17-20th June 2018) concerning the assessment of heat of reaction of Hydrothermal Carbonisation process. Chapter 4 reports the main research activity I performed concerning hydrothermal carbonisation of sewage sludge, providing the characterisation of solid and liquid phases and the assessment of their potential valorisation. Chapter 5 is a description of the system designed in order to perform Bio Methane Potential (BMP) tests: some preliminary tests on sewage sludge treated by means of Hydrothermal process are reported. Chapter 6 is the final chapter that gives a summary of the research, and highlights possible future developments in the field of sludge Hydrothermal Carbonisation.

Chapter 1

Hydrothermal Carbonisation of Sewage Sludge. A Review

This Chapter is a review on Hydrothermal Carbonisation process and its application for sewage sludge treatment. This chapter assesses also the application of the produced hydrochar and its energy balance.

Hydrothermal Carbonisation of Sewage Sludge. A Review

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1.0 Abstract

Hydrothermal Carbonisation (HTC) has recently emerged as a promising technology for sustainable sludge minimization and solid products valorisation, but no systematic review has been reported to date. HTC of sewage sludge was study for many different purposes: as a way to produce a new clean biofuel, as soil improver, as an adsorbent and as a source of phosphorous that is not renewable raw material. The aim of this work is to assess the application of the produced hydrochar and its energy balance in order to apply the circular economy concept generating a valuable product from a waste in a sustainable way.

Keywords: Hydrothermal Carbonisation; Sewage Sludge; Hydrochar; Hydrochar applications.

1.1 Introduction

Conventional activated sludge (CAS) systems have been widely implemented to treat municipal wastewaters producing a significant amount of waste sludge. Its treatment represents up to 65 % of the operational costs of wastewater treatment plants (WWTPs) (Ferrentino et al. 2016). Many technologies have been developed in order to minimize the final sludge disposal. Among these processes, HydroThermal Carbonisation (HTC) has emerged as a promising technology for efficient sludge minimization and relevant products valorisation (He et al. 2013). While other thermochemical processes such as pyrolysis and gasification, requires drying as pre-treatment, HTC takes place in water and is therefore well suited for wet organic waste, such as sludge, requiring lower temperature compared with pyrolysis and gasification. HTC produces a sterile, stable, enriched in carbon and energy material, namely hydrochar, that could be used as renewable biofuel, as soil amendment, as adsorbent in soil or water remediation and it could be produced in a sustainable way from several wet organic waste streams (Berge et al. 2013; Parshetti et al. 2013; Titirici et al. 2015). Another important advantage of HTC is the resulting reduction of mass and volume of the initial waste biomass, involving less disposal space, but, nowadays, research on HTC is more focused on the production of value-added products from waste stream (Berge et al. 2013). HTC process is carried out by heating biomass up to 180 – 250 ℃ in a suspension with water under saturated pressure for several hours, converting biomass into hydrochar, which can be easily separated from the HTC process wastewater due to its reduced polarity of surface, which increases consequently the dewaterability (Funke and Ziegler 2010; Basso et al. 2016; Lucian and Fiori 2017). Numerous studies focused on the characterization of hydrochar, which is biologically sterilized and exhibits a moderate calorific value, highly aromatic structures and mesoporous textures (He et al. 2013). The derived chars can be utilized as renewable biofuels (He et al. 2013; Parshetti et al. 2013; Kim et al. 2014; Zhao et al. 2014; Peng et al. 2016), as soil amendments to improve soil quality (Danso-Boateng et al. 2012; Zhang et al. 2014; Breulmann et al. 2017; Yue et al. 2017), as adsorbents (Alatalo et al. 2013; Saetea and Tippayawong 2013), as a tool for CO_2 sequestration due to the significant carbon fraction that remains within the hydrochar during the HTC process (Titirici et al. 2007), or as resources for phosphorous recycling and reclamation (Berge et al. 2013; He et al. 2013; Weber et al. 2014; Zhao et al. 2014). Many studies focused on the energy value of the hydrochar produced by sewage sludge. Nevertheless, the high moisture content could lead to a low thermal efficiency of the HTC process, definable as the ratio between the High Heating Value (HHV) of dried hydrochar and the

thermal energy required by the process, because a substantial amount of water per unit of mass of dry feedstock is treated (Lucian and Fiori 2017). To the best knowledge of the authors, no systematic review has been reported to date on the valorisation of sewage sludge by means of HTC. In the present review the current state of the art on HTC process waters is discussed, emphasizing the importance of HTC operating parameters, as well as the possible limits. In addition, future directions for HTC research in this field are outlined.

1.2 Characterization of Sewage Sludge

Sewage sludge, which is originated from the treatment of wastewater in the water line of WWTPs, is the residue generated during the primary, the secondary (waste activated sludge, WAS) and often the tertiary treatment. The produced sludge can be further processed in the sludge treatment line, where it can be stabilized and dewatered. Its characteristics depend on the type of wastewater (civil, industrial, agro-industrial,etc.), the type of WWTP and its operation strategies; in Figure 1.1 a tradition WWTP is reported. Mainly, the difference in composition between different sewage sludge lies in the percentage of carbon and inorganics. Primary sludge is known to be more biodegradable than WAS and digested sludge (Metcalf&Eddy 2003). On the contrary, WAS and stabilized (aerobically or anaerobically) material (digested sludge) are characterized by lower percentages of carbon, which can be respectively explained by the relatively high sludge retention time (SRT) in the biological processes in the water treatment line and in the anaerobic (or aerobic) digestion process to which the produced sludge is subjected in the sludge treatment line. The chemical composition of sewage sludge is important when considering the final disposal of both the processed sludge (hydrochar) and the process waters separated from the sludge during and afterwards the HTC treatment (Li et al. 2015). In particular, the distribution of organic carbon, nutrients, heavy metals, pesticides, hydrocarbons among the HTC product streams affects the management of the HTC final products. Finally, with the traditional sludge treatment techniques, a maximum solids content of about 20-30 % can reached, implying high transport costs and high disposal costs due to the high moisture of the sludge (75-80 %). Applying technologies that can drastically reduce the amount of sludge to be disposed of at a low cost is challenging, in this sense HTC is a very promising technology.

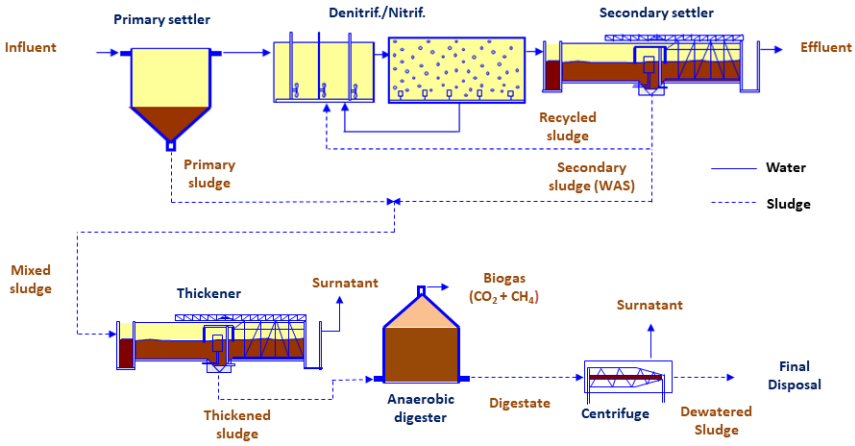

Figure 1.1: a traditional WWTP scheme.

1.3 Hydrothermal Carbonization Process: Properties of water, chemistry, kinetics and operative parameters

Operative parameters and, as a consequence, the properties of water at different states, such as ion product, density, dielectric constant and hydrogen bonding, affect the yields of gas, liquid and solid products of hydrothermal biomass conversion (Jin et al. 2014), so in this section operative parameters, the properties of water and the main reaction mechanisms are briefly summarized.

1.3.1 Properties of Water

The ion product K_w, that is the product between H^+ and OH^- concentrations, at environmental conditions is $10^{-14}\ mol^2\ kg^{-2}$ and increases up to $10^{-11} mol^2\ kg^{-2}$ at 300 ℃ at constant pressure involving an enhancement of acid and base catalysed reaction (Brunner 2014; Jin et al. 2014). The ion product K_w is affected by water density following Eq.1.3.1:

$$\log K_w = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \left(E + \frac{F}{T} + \frac{G}{T^2}\right)\log \rho \tag{1.3.1}$$

Where T is temperature in K, ρ is density in $g\ cm^{-3}$ and $A - G$ are parameters. Water density decreases from 1 $g\ cm^{-3}$ at environmental conditions to 0.8 $g\ cm^{-3}$ at 300 ℃. It is not clear if water density affects reaction mechanisms, especially at higher temperature where water density drops to 0.15 $g\ cm^{-3}$ at 450 ℃, only varying the ion product (Jin et al. 2014). Another important property of water is the dielectric constant;

this property of water is defined as the ratio between the permittivity of a substance and the permittivity of vacuum; the dielectric constant of water at environmental conditions is 78.5 involving the use of water as solvent for polar substances. Increasing the temperature, dielectric constant drops reaching values of 44 at 150 ℃, 35 at 200 ℃, 27 at 250 ℃ and 20 at 300 ℃, that are similar compared with dielectric constant of organic solvent, such as methanol (dielectric constant of methanol is 33 at 25 ℃), involving that water could be used as organic solvent (Jin et al. 2014). On the contrary, increasing temperature and accordingly decreasing water density, the hydrogen bonding becomes weaker and less persistent suggesting that molecules of water could participate as a catalyst or as a source of hydrogen for some reaction steps (Jin et al. 2014).

1.3.2 Chemistry

The main HTC reaction mechanisms are *hydrolysis, dehydration, decarboxylation (and decarbonylation), condensation - polymerization, and aromatization* (Funke and Ziegler 2010; Libra et al. 2011; Volpe and Fiori 2017; Volpe et al. 2018; Fang et al. 2018). In Funke and Ziegler (2010) it is stated that these reaction mechanisms can occur in parallel and their development is affected by the initial biomass; furthermore, the reaction pathway is not completely known and understood yet. Figure 1.2 provides a possible hydrochar formation pathways during HTC of sewage sludge.

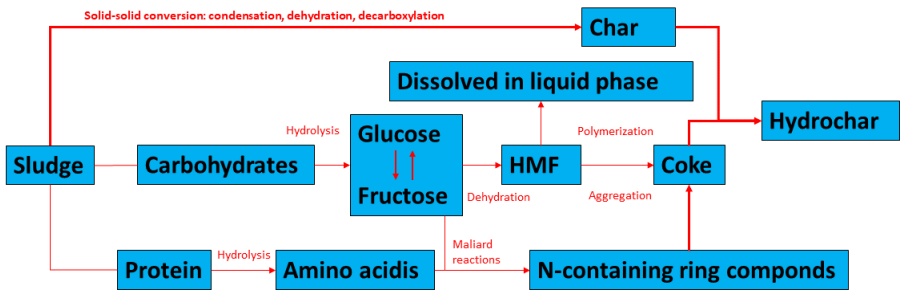

Figure 1.2: possible hydrochar formation pathways of HTC of sewage sludge (He et al. 2013; Wang et al. 2018).

Hydrolysis is one of the major reactions of hydrothermal conversion and can happen both in acid and base catalysed reactions leading to the cleavage of mainly ester and ether bonds of the macromolecules. There are three possible reaction paths: acid hydrolysis where the formation of conjugated acid leads to bond cleavage; base hydrolysis where hydroxyl ion cleaves O bridge; water catalysed reaction that involves H_2O adsorption (Funke and Ziegler 2010; Jin et al. 2014). Chemical *dehydration*

involves lowering the H/C and O/C ratios of the initial biomass and it is generally explained by elimination of hydroxyl groups (Funke and Ziegler 2010; Jin et al. 2014). Concerning *decaboxylation* and *decarbonylation*, hydrothermal treatment causes a partial elimination of carboxyl groups. As showed in Eq.1.3.2, carboxyl and carbonyl groups degrade, above 150 ℃, yielding CO_2 and CO, respectively (Funke and Ziegler 2010; Jin et al. 2014).

$$\begin{aligned} HCCOH &\rightarrow H_2 + CO_2 \\ HCCOH &\rightarrow H_2 + CO \end{aligned} \tag{1.3.2}$$

Berge et al. (2011) proposed the stoichiometric reaction described in Eq.1.3.3 where digestate is converted mainly in char, dissolved organics and CO_2. Following Eq.1.3.3, the same authors computed the heat of reaction of HTC of digestate and they found a value of -0.75 $MJ\ kg^{-1}_{feedstock}$, comparable with -1 $MJ\ kg^{-1}_{feedstock}$ associated with the heat of reaction of cellulose treated by means of HTC process (Libra et al. 2011).

$$\begin{aligned} &Digestate \rightarrow char + dissolved\ organics + CO_2 \\ &H_{1.77}O_{0.47}N_{0.14}S_{0.01} \rightarrow 0.40CH_{1.67}O_{0.21}N_{0.063}S_{0.01} + \\ &+0.60CH_{1.8}O_{0.64}N_{0.20}S_{0.001} + 6.5 \times 10^{-6}CO_2 \end{aligned} \tag{1.3.3}$$

Dehydration, decarboxylation and decarbonylation reactions lead to the creation of unsaturated fragments of bio-macromolecules that could be highly reactive and join together mainly by condensation *polymerization*, process in which two molecules react involving the loss of a molecule of water mainly (Funke and Ziegler 2010). At high temperature and pressure *aromatisation* can occur leading to the formation of aromatic structures and the presence of these structures can involve a decrease in carbon content of hydrochar (Funke and Ziegler 2010). Other possible mechanisms that can occur in HTC process are: *demehylation*, where phenol join a cathecol-like structure leading to the removal of a methyl group; *transformation reactions* that can occur when there are some stable compounds with a crystalline structure and oligomer fragments that do not hydrolyse and consequently polymerisation can't occur; *pyrolytic reactions* (above 200 ℃) where biomacromolecules carbonise because they precipitate with condensing fragments, so contact with H_2O can't occur; in the end *Fisher-Tropsch-type* reactions can also occur, but their role is not understood yet although this kind of mechanism has been observed (Funke and Ziegler 2010; Basso et al. 2013). In general, the main reactions occurring during HTC are dehydration and decarboxylation (Funke and Ziegler 2010), that have both negative enthalpy, so HTC is slightly exothermic (Funke and Ziegler 2011; Merzari et al. 2018). For this reason,

the energy released progressively increases with stronger carbonization and, correspondingly, the atomic ratios H/C and O/C decrease. Globally, de-oxygenation occurs: the oxygen is released in the form of carbon dioxide (CO_2) - decarboxylation - and water (H_2O) - dehydration. De-oxygenation is important because it reduces the polarity of the hydrochar surface, which increases consequently the dewaterability of the produced hydrochar.

1.3.3 Kinetics

In recent years, many studies have focused on how HTC process parameters affect the characteristics of hydrochar. Baratieri et al. (2015) suggested a simple kinetics model for HTC of grape marc based on a two-step reaction mechanism: the initial feedstock (A) forms an intermediate product (B) that partially converts to the final product C, namely hydrochar. The model takes also into account other two reactions in parallel in order to consider the formation of gaseous products. The model lacked in considering the organics present in the HTC liquid phase, so Lucian et al. (2018) proposed a new kinetic model for HTC of grape marc. Figure 1.3 shows the scheme used in the kinetics model which describes the reaction pathways of HTC.

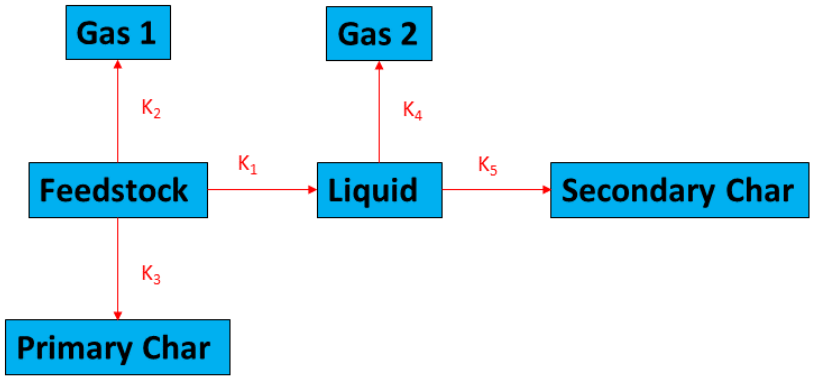

Figure 1.3: kinetic model scheme (Lucian et al. 2018).

The first reaction step models the hydrolysis and dissolution processes. These liquid products can react leading to stable liquid compounds or highly reactive intermediates such as 5-HMF. These intermediates can back polymerize producing "secondary char" (reaction 5) (Lucian et al. 2018; Volpe and Fiori 2017). In parallel, dehydration of initial feedstock occurs (reaction 3). As a consequence, there is a reduction of the H/C and O/C ratios in the produced hydrochar due to water removal. After dehydration, decarboxylation and decarbonylation reactions occur

(Funke and Ziegler 2010; Lucian et al. 2018). Decarboxylation and decarbonylation involve the elimination of CO_2 and CO and are modelled through reaction 2. In the end, liquid compounds resulting from hydrolysis could generate small gaseous molecules, mainly CO_2 (reaction 4), or back - polymerize and condense as a solid phase (reaction 5) as already stated (Lucian et al. 2018). The kinetics parameters k_i in Figure 1.3 are the kinetics constants of the five reactions and are expressed through the Arrhenius equation Eq.1.3.4:

$$k_i = k_{0,i} e^{-\frac{E_{a,i}}{RT}} \qquad i = 1, ..., 5 \tag{1.3.4}$$

The kinetics model is a system of non-linear differential equations expressed in Eq.1.3.5:

$$\begin{array}{l} \frac{\partial C_B}{\partial t} = -k_1 C_B - k_2 C_B - k_3 C_B \\ \frac{\partial C_L}{\partial t} = k_1 C_B - k_4 C_L - k_5 C_L^n \\ \frac{\partial C_{G1}}{\partial t} = k_2 C_B \\ \frac{\partial C_{HC1}}{\partial t} = k_3 C_B \\ \frac{\partial C_{G2}}{\partial t} = k_4 C_L \\ \frac{\partial C_{HC2}}{\partial t} = k_5 C_L^n \end{array} \tag{1.3.5}$$

Where t is the reaction time and C_B, C_L, C_{G1}, C_{HC1}, C_{G2} and C_{HC2} are the molar concentration expressed in $mol\ L{-}1$ of carbon respectively in **B**iomass, **L**iquid phase, **G**as **1**, primary hydrochar (HC1), **G**as **2** and secondary hydrochar (HC2). The carbon molar concentration in component X (C_X), is expressed in Eq.1.3.6:

$$C_X = \frac{n_{C,X}}{(V_B + V_W)} \tag{1.3.6}$$

Where $n_{C,X}$ are the moles of carbon in component X and term $V_B + V_W$ is the sum of the volumes in L of biomass as received and distilled water added to the system. An error function $F(k_i, n)$, where here n is the reaction order of reaction 5, is expressed in Eq.1.3.7 and has as input variables experimental data (apex: "exp") obtained at different HTC reaction times and the corresponding data computed by the model (apex: "mod"). The subscript j refers to the various reaction times at which experimental data are available. $F(k_i, n)$ was thus minimized in order to get the kinetics parameters k_i and n (Lucian et al. 2018).

$$\begin{array}{rcl} F(k_i, n) & = & \sum_j \left| C_{S,j}^{exp} - C_{S,j}^{mod} \right| + \left| C_{L,j}^{exp} - C_{L,j}^{mod} \right| + \\ & + & \left| C_{G,j}^{exp} - C_{G,j}^{mod} \right| \end{array} \tag{1.3.7}$$

Specific studies on HTC of sewage sludge reaction kinetics were also conducted (Danso-Boateng et al. 2013). In particular, in Danso-Boateng et al. (2013) the authors studied a kinetic model for HTC of primary sewage sludge and faecal waste, taking into account the influence of reaction temperature and time using a first-order reaction rate and Arrhenius equations to model the solids decomposition kinetics. The reaction rate is function of temperature and solids content, while temperature affects the degree of conversion to hydrochar. The initial reacting solids dependence on the reaction rate can be expressed as a first-order differential rate equation Eq.1.3.8.

$$-r = \frac{dm_t}{dt} = k\ m_t \tag{1.3.8}$$

that leads to Eq.1.3.9 through separation and integration.

$$-\ln \frac{m_t}{m_0} = k\ t \tag{1.3.9}$$

where r is the reaction rate, m_t is the mass of hydrochar at reaction time (t), m_0 is the initial mass of solids at initial conditions, both expressed on a dry weight basis, k is the reaction rate constant (min^{-1}), and t is the reaction time (min). In terms of reactant conversion Eq.1.3.10 can be expressed:

$$X = \frac{m_t - m_\infty}{m_0 - m_\infty} \tag{1.3.10}$$

where X is the conversion of faecal solids to hydrochar, m_∞ is the equilibrium mass of solids (or hydrochar) over time $t = \infty$. So the variation of X in function of the time can be expressed in Eq.1.3.11:

$$\frac{dX}{dt} = -k\ X \tag{1.3.11}$$

The solution of Eq.1.3.11 leads to Eq.1.3.12:

$$X\,(t) = e^{k\ t} \tag{1.3.12}$$

The temperature affects the degree of conversion (Y) to hydrochar (at equilibrium) which is expressed in Eq.1.3.13.

$$Y = \frac{m_t}{m_0} \times 100 \tag{1.3.13}$$

Arrhenius equation was used to express the correlation between temperature and reaction rate (Eq.1.3.14).

$$K = A\ e^{\frac{E}{RT}} \tag{1.3.14}$$

where, A is the pre-exponential factor (min^{-1}), E is the activation energy ($J\ mol^{-1}$), R is the gas constant (8.314 $J\ mol^{-1}\ K^{-1}$), and T is the temperature (K). Danso-Boateng et al. (2013) computed the kinetic parameters, namely activation energy and pre-exponential factor: the activation energy for faecal waste was 77.8 $kJ\ mol^{-1}$ and its pre-exponential factor was $1.5 \times 10^7\ min^{-1}$, while the activation energy for primary sludge was 70.4 $kJ\ mol^{-1}$ and its pre-exponential factor was $4.0 \times 10^6\ min^{-1}$. The higher activation energy of faecal waste compared with primary sludge involves a higher temperature required to initiate the decomposition of faecal waste to produce hydrochar than that required for primary sludge.

1.3.4 Operative Parameters

The main parameters of HTC are: temperature, pressure, residence time, pH, feedstock composition and biomass to water ratio (b/w) (Basso et al. 2013).

1.3.4.1 Temperature

Temperature represents the most influence parameter of HTC process: high temperatures lead to higher reaction affecting directly the kinetics of the reactions and determining water properties leading to ionic reactions mainly in the subcritical region (Funke and Ziegler 2010; Nizamuddin et al. 2017; Wang et al. 2018). Moreover, temperature affects directly the number of initial feedstock compounds that can be hydrolysed (below 180 ℃ carbonization occurs with difficulty). In the end, increasing temperature leads to an enhancement in carbon content of the hydrochar and consequently its energy content and calorific value, while the hydrochar yield general decreases: increasing temperature enhances dehydration and the decarboxylation reaction rate, so consequently the O/C and H/C ratios involving the enhancement of carbon content of the hydrochar (Basso et al. 2013; Nizamuddin et al. 2017; Wang et al. 2018). Moreover, higher temperatures lead to increasing liquid and gasses yields, involving a decrease of hydrochar yield due to the degradation of part of the char produced (Basso et al. 2013). Table 1.1 reports a literature review of applied temperature of HTC of different kind of sludge ranging from 180 ℃ to 280 ℃.

1.3.4.2 Pressure

Pressure affects reactions according to the principles of LeChatelier, so reaction equilibrium shifts to solid and liquid phases at rising reaction

pressure simultaneously to reactants with a lower number of moles, involving a decreasing reaction rate of dehydration and decarboxylation reactions. Pressure is mostly considered to be an indirect parameter of the process, because it is strongly dependent on the temperature and, in order to develop HTC, pressure should be such that to maintain water in the liquid phase: if a close system is heated above 100 ℃ contains biomass and water, the resulting pressure will be higher than the saturated vapour pressure due to the formation of gasses as a consequence of decarboxylation, so water is maintained at liquid state (Basso et al. 2013; Funke and Ziegler 2010; Nizamuddin et al. 2017). In the end, pressure affects strongly investment costs for pressure equipment (Funke and Ziegler 2010).

1.3.4.3 Residence Time

The residence time is interesting especially for practical processing design and strongly affects thermal and energy consumptions. It usually ranges between some minutes and several hours and affects process severity. Many authors reported that increasing residence time of the HTC process generally results in a higher carbon content of the hydrochar and, consequently, higher calorific value of the solid product. Moreover, in many works it is stated that residence time also reduces the yield of the hydrochar, promoting the formation of higher quantities of water soluble compounds (Basso et al. 2013; Funke and Ziegler 2010; Nizamuddin et al. 2017; Wang et al. 2018). In Wang et al. (2018) it is stated that long residence time can lead to the polymerization of fragments solved in the liquid phase involving the formation of secondary hydrochar with a poly - aromatic structure. Residence time affects strongly secondary hydrochar formation, especially for lignocellulose feedstock, because dissolved monomers required extensive polymerization. On the other hand, temperature affects the behaviour of non-dissolved monomers, so residence time allows the control of the degree of polymerization of the soluble monomers during the process (Wang et al. 2018). Table 1.1 reports a literature review of applied residence time of HTC of different kind of sludge ranging from 15 min up to 24 h.

1.3.4.4 pH

During the HTC reaction, typically, the pH drops due to the formation of several acidic compounds, such as acetic, formic, levulinic and lactic acid, so HTC process is considered autocatalytic (Funke and Ziegler 2010; Wang et al. 2018). Generally acidic conditions catalyze the carbonization of biomass, improving the hydrolysis rate of macromolecules, while

the influence on decarboxylation or condensation polymerization is not known yet (Basso et al. 2013). The addition of acids has an influence on the kinetics of the reaction as well as on the reaction conditions. Weakly acid conditions promote the overall rate of the HTC and increase the carbon yield as well as carbon content of the hydrochar. In the end, acids and alkali can be added and used as a catalyst during HTC, involving an increase in H^+ or OH^- concentration that leads to elevated ionic strength, promoting the reaction rate or the desired reaction pathway (Wang et al. 2018).

1.3.4.5 Solid Load

The solid load is the ratio of biomass to water defined in Eq.1.3.15. A high b/w can promote a lower overall residence time, by increasing the rate at which the concentration of monomers is raising, which allows an earlier polymerization (Funke and Ziegler 2010).

$$\frac{b}{w} = \frac{mass_{dry\ biomass}}{mass_{biomass\ moisture} + mass_{added\ water}} \tag{1.3.15}$$

In Wang et al. (2018) it is stated that high b/w values lead to partly polymerization due to the incomplete hydrolysis of macromolecules. In the end, high b/w required more thermal energy and a long residence time in order to hydrolyse polymers and produce enough monomers in order to reach equilibrium and finally precipitate as hydrochar (Wang et al. 2018). Table 1.1 reports a literature review of applied b/w of HTC of different kind of sludge ranging from 3 % up to above 30 %.

1.3.4.6 Feedstock Composition

In order to treat wet organic waste or biomass, HTC process is a better treatment compared to pyrolysis or biological process, due its independence on the initial feedstock characterisation. HTC can treat the biomass as received, without drying pre-treatment, and toxic compounds don't affect the process like for biological processes (Basso et al. 2013). On the other hand, initial feedstock composition affects the final hydrochar characterisation: if the inlet biomass has low carbon content and high ashes content the resulting hydrochar will not be an improved biofuel. Table 1.2 reports a literature review of different kind of sludge treated by means of HTC process. The characterisation of sludge is mainly in terms of ultimate and proximate analysis and its HHV. The king of sludge reported are: primary sewage sludge (PSS), digestate, Sewage sludge (SS), Dewatered sewage or activate sludge (DSS and DAS) and faecal sludge (FS).

1.3.4.7 Other Parameters

Heating rate is another operative parameter that could affects the HTC process: heat and mass transfer limitations can decrease with high heating rate and, as a consequence, the time for secondary reactions of the intermediate products is reduced (Wang et al. 2018). Another parameter that affects HTC process is the use of catalysts: hydrolytic agents or catalysts can improve the hydrolysis rate. Catalysts differ according to the hydrolysis process employed. In Nizamuddin et al. (2017) it is stated that acid catalysts are the most effective for hydrolysis, while basic catalysts inhibit the formation of hydrochar and promote the formation of liquid oil. In the end, the use of catalyst can lead to a reduction in terms of NO_x converting into nitrogen and water (Nizamuddin et al. 2017).

1.3.5 Hydrothermal Carbonisation Plants

Table 1.3 reports a literature review of reactor type and volume utilised in order to apply HTC of sewage sludge: the reactor are all at lab scale with volumes that range between 75 mL and 25 L and work only in batch condition. There are also some companies, such as TerraNova Energy and $AVA-CO_2$, which apply HTC of sewage sludge at pilot scale in the order of some thousand tons for year, and their reactor work in continuous or semi-continuous mode. Recently, TerraNova Energy has constructed a full scale plant in China treating 14 thousand tons of sludge for year. In the TerraNova Energy plant sludge is pre-processed in order to obtain particle size optimal for feeding the continuous reactor. Under pressure, the sludge flows through a winding tube connected to a heat exchanger in a contrary flow to the HTC product leaving the reactor in a parallel tube. Oil is used as the heat recovery agent. When sludge enters the reactor it is preheated to near reaction temperature and pressure (200 ℃, $>$ 20 bar). The sludge is also mixed with a catalyst or additive, and fed into the continuous reactor. A mixer ensures a homogeneous mixture and char particles slowly sink to the bottom of the tank, from where they are released through the heat exchanger. The process ends with mechanical dewatering and possible post-treatment (http://terranova-energy.com/en/). In the $AVA-CO_2$ plant the sludge is preheated in a designated mixing tank by combining sludge with both high and low pressure (recycled) steam as well as recycled process liquid. The slurry is transferred to one of several batch reactor tanks upon reaching reaction conditions (220-230 ℃, $>$ 22 bar). Reactions in the reactor tanks is facilitated by means of stirrer mechanism and the use of catalysts. Once hydrothermal treatment is complete, the slurry is leached from the HTC reactor by gravity and pumped to high and low pressure flash tanks where process energy can

Table 1.1: literature review of main operative parameters of HTC of different kind of sludge.

Feedstock	**Temperature**	**Residence time**	**b/w**	**Reference**
Primary Sewage Sludge (PSS)	180, 200 ℃	15, 30, 60, 120, 240 min	4.30%	(Danso-Boateng et al. 2015b)
Digestate	250 ℃	20 h	3.00%	(Berge et al. 2011)
Digestate	180, 200, 220, 250, 280 ℃	30 min	-	(Kim et al. 2014)
Digestate	220, 250 ℃	30 min	4.70%	(Aragón-Briceño et al. 2017)
Dewatered Activated Sludge (DAS)	180, 200, 220, 240 ℃	15, 30, 45 min	10.00%	(Zhao et al. 2014)
Secondary Sewage Sludge (SS)	250 ℃	15 min	-	(Parshetti et al. 2013)
Dewatered Sewage Sludge (DSS)	220, 260 ℃	60 min	10.70%	(Zhai et al. 2017)
Sewage Sludge (SS)	180, 190, 200, 210 ℃	30 min	16.6 - 32.6 %	(Yoshikawa and Prawisudha 2014)
Dewatered Sewage Sludge (DSS)	180, 220, 260 ℃	30, 60, 90, 360, 480 min	11.10%	(Peng et al. 2016)
Dewatered Activated Sludge (DAS)	210 ℃	4 h	25.00%	(vom Eyser et al. 2015)
Urban Sludge (US)	180, 210, 240, 270 ℃	60 min	7.10%	(Xu and Jiang 2017)
Primary Sewage Sludge (PSS)	180, 200 ℃	4, 8 h	-	(Breulmann et al. 2017)
Sewage Sludge (SS)	200 ℃	4 h	-	(Breulmann et al. 2017)
Digestate	200 ℃	30 min	23.50%	(Liu et al. 2017; Liu et al. 2018)
Faecal sludge (FS)	250 ℃	5 h	25.00%	(Fakkaew et al. 2018)
Dewatered Sewage Sludge (DSS)	200 ℃	4, 6 , 8, 10, 12 h	16.70%	(He et al. 2013)
Dewatered Activated Sludge (DAS)	220 ℃	60 min	11.10%	(Gai et al. 2016)
Sewage Sludge (SS)	270 ℃	120 min	11.10%	(Zhai et al. 2016)
Sewage Sludge (SS)	180, 240 ℃	30 min	10.00%	(Zhuang et al. 2018)
Digestate	205 ℃	7 h	25.2 – 31.4 %	(Escala et al. 2013)
Dewatered Sewage Sludge (DSS)	190, 205, 220 ℃	5, 7 h	9.90%	(Escala et al. 2013)
Digestate	250 ℃	60 min	11.10%	(Ekpo et al. 2016)
Sewage Sludge (SS)	190, 260 ℃	1, 6, 12, 18, 24 h	25%	(Zhang et al. 2014)

Table 1.2: literature review of different kind of sludge treated by means of HTC process.

Feedstock	**ASH** [%]$^{(a)}$	**VM** [%]$^{(a)}$	**FC** [%]$^{(a)}$	**C** [%]$^{(a)}$	**H** [%]$^{(a)}$	**N** [%]$^{(a)}$	**O** [%]$^{(a)}$	**S** [%]$^{(a)}$	**HHV** $[MJkg^{-1}]$	**Reference**
PSS	27.54	68.56	3.9	36.63	5.79	5.29	52.3	-	-	(Danso-Boateng et al. 2015b)
Digestate	35.9	55.9	8.2	32.6	4.8	5.5	20.3	0.92	15.5	(Berge et al. 2011)
DAS	18.51	78.49	2.01	51.2	6.64	8.85	31.94	1.37	18.82	(Zhao et al. 2014)
Digestate	26.06	66.87	7.07	38.55	6.46	8.05	46.5	0.44	16.5	(Kim et al. 2014)
SS	24.8	62.7	6.12	28.58	5.82	4.4	59.4	1.8	10.83	(Parshetti et al. 2013)
SS	33.41 - 69.36	25.46 - 55.42	4.18 - 11.17	50.88 - 69.19	5.80 - 8.37	3.58 - 9.39	18.86 - 34.76	-	7.10 - 19.68	(Yoshikawa and Prawisudha 2014)
DSS	49.85	47.49	2.66	25.03	4.21	4.86	15.31	0.74	10.97	(Peng et al. 2016)
Digestate	31.77	55.81	7.76	34.78	3.93	5.04	20.32	1.15	16.61	(Aragón-Briceño et al. 2017)
US	-	-	-	-	-	-	-	-	6.34	(Xu and Jiang 2017)
PSS	28.7	57	14.3	51.3	5.7	4.2	28.4	-	-	(Breulmann et al. 2017)
SS	31.5	46	22.5	44.9	5.2	4.5	31.8	-	-	(Breulmann et al. 2017)
Digestate	42.86	49.01	8.13	26.67	3.25	4	22.05	1.17	-	(Liu et al. 2017; Liu et al. 2018)
FS	31.30 - 33.80	57.0 - 60.0	9.70 - 1.20	37.80 - 38.10	5.00 - 5.50	3.00 - 3.50	19.40 - 19.52	1.40 - 1.60	13.50 - 14.10	(Fakkaew et al. 2018)
DSS	28.6	69.98	1.42	36.7	6.4	5.5	35.9	9.5	14.67	(He et al. 2013)
DAS	30.76	57.78	11.46	33.98	6.02	6.24	52.84	0.92	13.17	(Gai et al. 2016)
SS	-	-	-	25.03	4.21	4.86	15.31	0.74	-	(Zhai et al. 2016)
SS	56.5	39.2	4.2	21.6	3.7	3.4	14.3	0.5	9.67	(Zhuang et al. 2018)
Digestate	-	-	-	24.89	4.78	3.91	33.08	1.09	10.66	(Escala et al. 2013)
DSS	-	-	-	38.11	6.12	3.31	31.99	0.36	17.2	(Escala et al. 2013)
Digestate	61.2	34.4	3.3	18.3	2.9	2.7	14.6	0.3	7.8	(Ekpo et al. 2016)
SS	33.14	-	-	36.33	5.9	4.23	12.81	-	17.55	(Zhang et al. 2014)

[a]Weight Percentage Dry basis

be recovered in order to preheat sludge.

1.4 Hydrothermal Carbonization Products

The products resulting from HTC process are a solid phase enriched in carbon, namely hydrochar, a liquid phase with many organic compounds dissolved and a small quantity of gas mostly composed of CO_2, with traces of CO, CH_4, H_2 (Basso et al. 2015; Basso et al. 2016) and NH_3 Danso-Boateng et al. (2015b).

1.4.1 Solid Product - Hydrochar

Hydrochar is the solid phase, with H/C and O/C ratios lower than the original feedstock and its elemental composition is similar to lignite or sub-bituminous coal as showed in Figure 1.4.

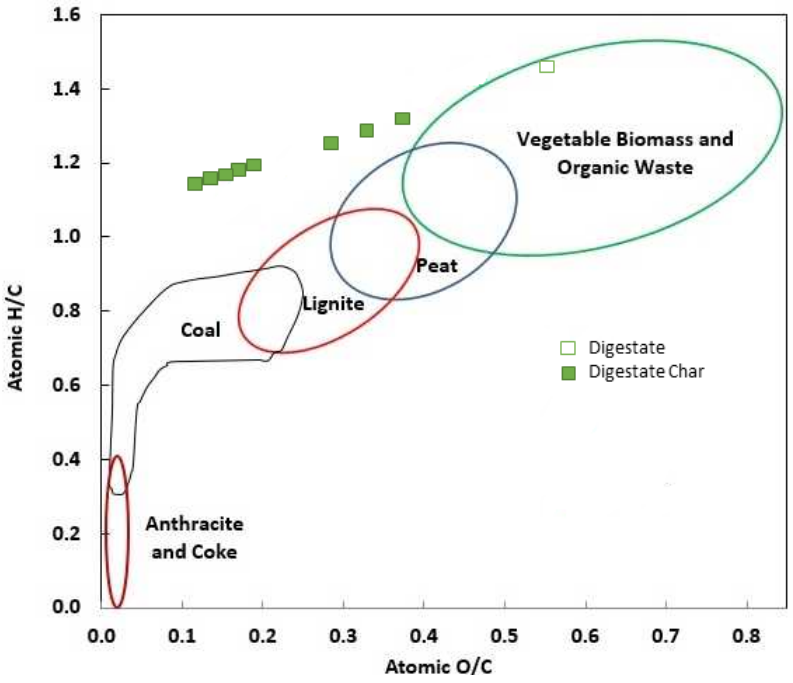

Figure 1.4: Van Krevelen diagram and its variation due to HTC process from Mumme et al. (2011).

Table 1.4 reports a literature review of hydrochar characterisation from HTC of different kind of sludge: as process severity increases, namely increasing temperatures and residence time, solid yields in general decrease; also H/C and O/C ratios decrease, resulting in greater energy

Table 1.3: literature review of reactor type and volume utilised in order to apply HTC of sewage sludge.

Reactor type	**Volume**	**Stirred**	**Notes**	**Reference**
Batch	250 mL	-	Separation liquid/solid by vacuum filtration 10 µm pores	(Danso-Boateng et al. 2015b)
Batch	160 mL	-	Separation liquid/solid by filtration 1 µm pores	(Berge et al. 2011)
Batch	500 mL	yes	-	(Zhao et al. 2014)
Batch	1000 mL	yes	-	(Kim et al. 2014)
Batch	500 mL	yes	-	(Parshetti et al. 2013)
Batch	500 mL	yes	-	Zhai et al. (2017)
Batch	20 L	yes	-	(Yoshikawa and Prawisudha 2014)
Batch	500 mL	yes	Separation liquid/solid by vacuum microfiltration	(Peng et al. 2016)
Batch	500 mL	-	-	(Aragón-Briceño et al. 2017)
Batch	0.1 and 5 L	yes	Separation liquid/solid by filtration 1 µm pores	(vom Eyser et al. 2015)
Batch	500 mL	yes	Separation liquid/solid by qualitative filtration	(Xu and Jiang 2017)
Batch	1 L	-	Separation liquid/solid by vacuum filtration 1.2 µm pores	(Fakkaew et al. 2018)
Batch	125 mL	-	Separation liquid/solid by washing + vacuum filtration	(He et al. 2013)
Batch	500 mL	-	Separation liquid/solid by vacuum filtration 0.45 µm pores	(Zhai et al. 2016)
Batch	2.5 L	yes	Separation liquid/solid by vacuum centrifuge	(Liu et al. 2017; Liu et al. 2018)
Batch	250 mL	yes	Separation liquid/solid by vacuum filtration 0.45 µm pores	(Zhuang et al. 2018)
Batch	25 L	yes	-	(Escala et al. 2013)
Batch	75 mL	-	Separation liquid/solid by filtration	(Ekpo et al. 2016)
Batch	1 L	-	Separation liquid/solid by filtration	(Zhang et al. 2014)

densification and higher heating value because most of the carbon of initial feedstock remains within the hydrochar up to 80 %, if compared with liquid and gases products (Basso et al. 2013). In Libra et al. (2011) is stated that the hydrochar could have a HHV ranging between 28.9 and 29.3 $MJ\ kg^{-1}$, corresponding to an increase of 1.50 - 1.71 of heating value of the original biomass, while, as reported in Table 1.4, the HHV of hydrochar from sludge can reach value just above 20 $MJ\ kg^{-1}$ at maximum. An explanation of the lower HHV compared with hydrochar from other feedstock is the high ash content, especially for stabilised sludge where the organic matter is converted into biogas through anaerobic digestion or carbon dioxide through aerobic digestion. Indeed, the hydrochar can have lower HHV compared with initial feedstock comparing Table 1.2 and Table 1.4; however, computing the carbon content and the HHV in dry ash free basis, it is possible to observe that carbon content and HHV increase compared with the initial sludge as expected from HTC process. Concerning other characteristics of the hydrochar, in Table 1.4 it is possible to observe that, in general, at increasing temperature and residence time ASH and VM tends to decrease, on the other hands FC tends to slightly increase. In some works ASH content reach values above 70 % leading to low HHVs also at high severity process conditions. In the end, hydrogen, nitrogen, oxygen and sulphur concentrations decrease at higher severity process conditions, leading to lower SO_x and NO_x emissions if hydrochar will be used as biofuel.

As shown in Figure 1.4 the final carbon content is a function of the initial carbon, oxygen and hydrogen content of the biomass. Compared to cellulose, the HTC of digestate generates hydrochar with higher H/C ratios and lower O/C ratios suggesting that HTC of digestate promotes more decarboxylation rather than dehydration. Chemically the hydrochar has a significant amount of functional groups compared to natural bituminous coals, but lower amounts in carboxyl and hydroxyl groups due to decarboxylation and dehydration leading to higher hydrophobicity and, as a consequence, higher dewaterability than the original feedstock / sludge (Basso et al. 2015). The improved dewaterability of sludge after HTC, is one of the best advantage of the process because also considering hydrochar as a waste, the volume of waste to dispose of can be reduced between three and four times. The dewaterability increases also due to the cleavage of bacterial walls that leads to the release of bound water as showed in Figure 1.5. Yoshikawa and Prawisudha (2014) found that moisture content after dewatering was between 50 and 60 % at 180 °C but values below 40 % can be reached with frame filter. The authors studied also the dewaterability in function of time and they found that moisture at 190 °C was 70 % after 10 minutes and decreased down to 60 % after 20 minutes, 55 % after 30 minutes, 50 % after 40 minutes and, in

Table 1.4: literature review of hydrochar characterisation from HTC of sewage sludge.

Feeds.	Temp. [°C]	Res. Time	ASH [%][a]	VM [%][a]	FC [%][a]	C [%][a]	H [%][a]	N [%][a]	O [%][a]	S [%][a]	Solid yield [%]	HHV [MJ kg^{-1}]	Reference
PSS	180	30 – 240 min	33.46 – 39.17	57.37 - 63.01	1.92- 3.53	37.83 – 38.29	5-19 - 5.48	2.75 - 4.11	52.58 – 53.77	-	61.87 - 70.74	17.64 – 18.26	(Danso-Boateng et al., 2015)
	200	15 – 240 min	35.87– 38.94	55.33 - 63.14	1.00- 5.73	37.69 – 39.24	5.12- 5.40	2.55 - 3.14	53.09 – 54.08	-	60.54 - 69.32	17.52 – 18.65	
Dig.	250	20 h	55.80	34.50	6.40	27.80	3.90	2.00	7.80	0.77	47.10	13.70	(Berge et al., 2011)
DAS	180	15 – 45 min	22.02- 25.56	69.69 - 74.47	2.06– 3.20	52.19 – 55.31	6.52– 6.69	8.98- 9.08	27.55 - 30.81	1.36– 1.39	90.59 – 96.94	18,30 – 19.43	(Zhao et al., 2014)
	200	15 - 45 min	24.67 - 27.85	67.56 - 71.16	3.06– 3.60	55.07 – 59.23	6.65 - 6.72	7.98- 9.29	24.84 - 27.62	1.26 - 1.30	88.40 – 93.26	18,90 – 19.86	
	220	15 - 45 min	26.61– 29.23	66.59 - 68.94	3.02– 3.97	59.31 – 62.31	6.29 - 6.68	8.24 - 9.03	21.47 – 24.13	1.18- 1.20	84.43 – 90.75	19,74 -20.02	
	240	15 - 45 min	29.83– 34.68	57.42 - 64.63	5.12 - 7.42	61.29 – 67.96	5.71 - 6.26	8.19 - 8.95	16.25 - 21.93	1.29 - 1.56	78.14 – 85.16	19,86 – 20.17	
Dig.	180	30 min	29.35	62.28	8.37	39.98	5.92	7.18	46.68	0.24	93.9	17.3	(Kim et al., 2014)
	200	30 min	29.57	61.13	9.30	40.39	5.78	7.04	46.59	0.20	92.6	17.5	
	220	30 min	33.31	57.19	9.50	41.60	5.41	6.10	46.67	0.22	88.7	18.3	
	250	30 min	38.91	50.39	10.70	45.23	4.78	6.14	43.66	0.19	83.4	20.2	
	280	30 min	40.02	47.28	12.70	48.45	4.13	4.94	42.47	0.01	80.4	22.4	
SS	250	15 min	40.46	41.72	13.89	40.08	4.43	2.19	52.45	0.85	-	15.82	(Parshetti et al., 2013)
DSS	220	60 min	60.32	30.32	9.36	22.31	3.31	2.17	11.36	0.52	57.71	9.64	(Zhai et al., 2017)
	260	60 min	65.63	24.68	9.69	22.72	2.89	1.67	6.59	0.50	53.02	10.11	
SS	190	30 min	38.01- 70.8	24.84- 50.82	4.36- 10.37	48.54- 65.42	5.60- 8.12	3.41- 8.54	23.05- 37.42	-	-	6.77-19.34	(Yoshikawa and Prawisudha, 2014)
	200	30 min	40.05- 71.9	23.81- 50.01	4.20- 9.50	46.23- 63.10	5.50- 8.03	3.34- 8.36	25.53- 39.00	-	-	6.68-18.9	
DSS	180	30 min	68.47	22.18	9.15	21.23	3.51	1.64	4.27	0.67	66.18	10.80	(Peng et al., 2016)
	220	30 min	72.02	18.81	9.17	19.62	3.22	1.32	3.27	0.55	60.58	10.07	
	260	30 – 480 min	59.53- 62.46	22.61- 34.33	6.14- 13.24	19.90- 24.49	3.24- 3.92	1.24- 1.59	4.51- 10.54	0.51- 0.67	59.53- 69.74	9.80-12.06	
Dig.	220	30 min	45.11	43.82	9.05	33.21	3.91	2.01	14.66	1.09	73.40	14.33	(Aragón-briceño et al., 2017)
	250	30 min	36.88	51.11	9.21	38.03	4.89	4.23	14.78	1.19	56.80	17.80	
US	180	60 min	-	-	-	-	-	-	-	-	88.73 - 92.04	4.63 - 5.66	(Xu and Jiang, 2017)
	210	60 min	-	-	-	-	-	-	-	-	86.11	5.27	
	240	60 min	-	-	-	-	-	-	-	-	77.93	4.38	
	270	60 min	-	-	-	-	-	-	-	-	61.44	3.99	
PSS	180	4 h	33.50	52.50	14.00	58.60	5.70	3.30	21.30	-	-	-	(Breulmann et al., 2017)
	200	4 – 8 h	33.40- 33.80	51.40 - 52.40	14.20- 14.80	55.90 - 57.30	5.50– 5.70	2.60 – 2.90	22.20 – 23.20	-	-	-	
SS	200	4 h	34.00	49.70	16.30	49.40	4.90	4.70	27.10	-	-	-	
Dig.	200	30 min	58.54	31.33	10.13	23.40	2.36	2.06	12.54	1.10	-	-	(Liu et al., 2017)
FS	250	5 h	42.90– 44.80	39.80 – 43.70	12.60– 14.60	38.80 – 39.70	4.10 – 4.50	1.90 – 2.00	9.13 – 9.56	1.20 – 1.30	70.0 – 73.0	19.3 – 19.9	(Fakkaew et al., 2018)
DSS	200	4 – 12 h	43.89 - 46.69	45.00 - 50.64	5.47 – 8.31	32.50 – 33.30	4.10 – 4.40	2.10 – 2.20	16.90 – 18.50	3.80 – 3.90	-	14.37 – 15.09	(He et al., 2013)
DAS	220	60 min	52.58	31.74	15.68	43.58	4.79	9.52	42.63	1.03	-	16.21	(Gai et al., 2016)
SS	180	30 min	72.5	24.70	2.80	13.90	2.30	1.90	9.00	0.40	77.1	10.68	(Zhuang et al., 2018)
	240	30 min	81.0	16.80	2.20	9.70	1.80	1.20	6.00	0.30	70.2	8.84	
Dig.	205	7 h	-	-	-	25.86 - 25.56	4.06 – 4.14	3.83 – 4.00	28.24 – 27.59	1.15 – 1.16	-	-	(Escala et al., 2013)
DSS	190	5 h	-	-	-	40.95	6.03	3.60	28.82	0.37	-	-	
	205	5 - 7 h	-	-	-	40.22 – 41.12	5.72 – 5.93	2.30 – 2.76	26.73 – 28.04	0.36 – 0.43	-	-	
	220	5 h				41.15	5.80	2.69	26.98	0.38	-	-	
Dig.	250	60 min	81.40	17.40	1.10	10.00	1.40	0.60	6.40	0.20	-	4.30	(Ekpo et al., 2016)
SS	190	1 -24 h	46.65 – 50.80	-	-	35.92 – 36.74	4.93 – 5.12	1.73 – 1.87	4.03 – 7.96	-	-	16.74 – 17.24	(Zhang et al., 2014)
	260	1 – 24 h	49.85 –51.85	-	-	36.75 – 38.60	5.01 – 5.31	1.75 – 1.92	3.11 – 4.25	-	-	17.24 – 18.33	

*Weight Percentage Dry basis

the end, just below 50 % after 50 minutes. Similar values were found by Escala et al. (2013): treating stabilised sludge at 205 ℃ for 7 h the final moisture content after dewatering was 48 %, while treating not stabilised sludge at same conditions the final moisture content after dewatering was 30 %. In the end, Kim et al. (2014) studied the dewaterability of sludge

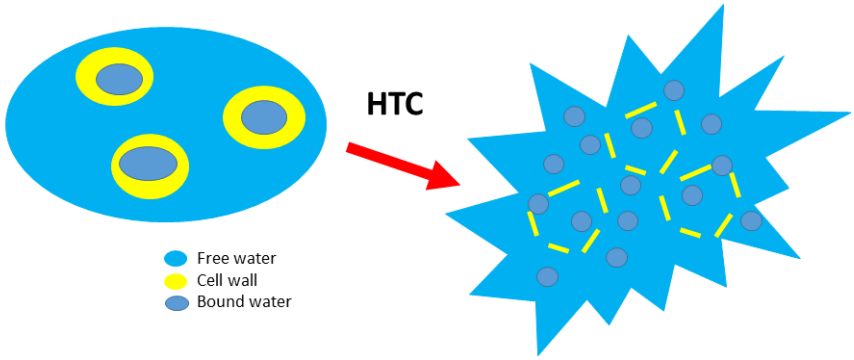

Figure 1.5: an explanation of the improved dewaterability of sludge (Yoshikawa and Prawisudha 2014).

after HTC treatment in term of capillary suction time (CST) that is an indirect measurement of the dewaterability of sludge: the test provides a quantitative measure (in seconds) of how readily sludge releases water. Kim et al. (2014) found that the CST of raw sludge was 72.03 s, while after the hydrothermal treatment, the CST of the hydrochar decreased to 15.35 s, 10.9 s, and 10.15 s at 180 ℃, 220 ℃, and 250 ℃, respectively. The CST results confirmed that the physical structure of the sludge was converted.

1.4.1.1 Nutrients

In general, the phosphorous content in the hydrochar tends to increase with the severity of the process (Breulmann et al. 2017; Ekpo et al. 2016; Escala et al. 2013; Sun et al. 2013), while nitrogen content of the hydrochar slightly decreases as report in Table 1.4. Concerning other nutrients such as Na and K, they always decrease significantly after HTC process, due to their high solubility in water since they are first group metals (Breulmann et al. 2017; Danso-Boateng et al. 2015b; Escala et al. 2013; Liu et al. 2017; Parshetti et al. 2013; Sun et al. 2013). Concerning second group metals, instead, there is not a clear trend, so the concentration of Ca and Mg can both slightly increase (Breulmann et al. 2017; Escala et al. 2013; Liu et al. 2017; Sun et al. 2013) or decrease (Danso-Boateng et al. 2015b; Parshetti et al. 2013; Sun et al. 2013).

1.4.1.2 Heavy Metals

Table 1.5 reports compost limits in different countries since nowadays there isn't a legislation concerning hydrochar. Many countries haven't a limit for As, but in general HTC lead to a decreasing of As concentration (Breulmann et al. 2017; Escala et al. 2013; Zhang et al. 2014). Concerning Cd, the limit in general is low and it seems that HTC slightly increases Cd concentration, so the initial concentration in the sludge strongly affects the use of hydrochar as soil improver (Breulmann et al. 2017; Escala et al. 2013; Zhang et al. 2014; Liu et al. 2018). Similar behaviour for Cr, where HTC slightly increases Cr concentration, so the initial concentration in the sludge strongly affects the use of hydrochar as soil improver (Breulmann et al. 2017; Escala et al. 2013; Zhang et al. 2014; Liu et al. 2018; Xu and Jiang 2017). Concerning Cu, the limit in general is not low and it seems that HTC both increases (Breulmann et al. 2017; Escala et al. 2013; Zhang et al. 2014; Liu et al. 2018) and decreases Cu concentration (Parshetti et al. 2013; Xu and Jiang 2017). Similar discourse for Pb: some authors found that HTC increases Pb concentration (Breulmann et al. 2017; Escala et al. 2013; Zhang et al. 2014; Liu et al. 2018), other stated that Pb concentration decreased (Sun et al. 2013; Xu and Jiang 2017). Concerning Hg, the limit is very low and it seems that HTC slightly increases Hg concentration or doesn't affect it, so the initial concentration in the sludge strongly affects the use of hydrochar as soil improver as for Cd (Breulmann et al. 2017; Escala et al. 2013; Liu et al. 2018). Concerning Ni, the limit is not low and it seems that HTC slightly increases Ni concentration or doesn't affect it, only Parshetti et al. (2013) found that Ni concentration decreased, so the initial concentration in the sludge strongly affects the use of hydrochar as soil improver (Breulmann et al. 2017; Escala et al. 2013; Liu et al. 2017; Liu et al. 2018). In the end, Zn concentration has high limit, but also here a clear trend of HTC wasn't found: some authors found that Zn concentration increased after HTC (Breulmann et al. 2017; Escala et al. 2013; Zhang et al. 2014; Liu et al. 2018; Sun et al. 2013) other stated that Zn concentration decreased (Parshetti et al. 2013; Sun et al. 2013; Xu and Jiang 2017).

1.4.2 Liquid Product

After HTC, in general, the HTC resulting process water has significant loads of various organic and inorganic compounds present in the liquid phase. In general, the organic compounds are mainly organic acids, sugars and the derivatives of both sugars and lignin (Basso et al. 2013). The concentration of these materials, often denoted as Total Organic Carbon (TOC) otherwise Chemical Oxygen Demand (COD), typically increases

Table 1.5: different legislations concerning bio-solid and composting ("Italian Law 75/2010, Norms Concerning fertilizers"; (Libra et al. 2011)).

	As $[mgkg^{-1}]$	**Cd** $[mgkg^{-1}]$	**Cr tot** $[mgkg^{-1}]$	**Cu** $[mgkg^{-1}]$	**Pb** $[mgkg^{-1}]$	**Hg** $[mgkg^{-1}]$	**Ni** $[mgkg^{-1}]$	**Zn** $[mgkg^{-1}]$
Austria - Compost		4	150	400	500	4	100	1000
Belgium - Compost		1	70	90	120	0.7	20	280
Denmark - Compost		1.2			120	1.2	45	
Germany - Compost		1.5	100	100	150	1	50	400
Spain - Compost		40	750	1750	1200	25	400	4000
Italy - Compost		1.5		230	140	1.5	100	500
USA - Biosolid	75	85		4300	840	57	420	7500

as reaction severity increases as reported in Table 1.6 and in Basso et al. (2015); also the b/w strongly affects the final TOC or COD of the HTC liquid, because higher solid load involves higher amount of organic compounds that can be solubilised. In order to increase the overall energy balance, many studies focused on the anaerobic valorisation of HTC liquor (Aragón-Briceño et al. 2017; Fakkaew et al. 2018; Danso-Boateng et al. 2015a; Wirth et al. 2015).

Danso-Boateng et al. (2015b) reported also a detailed list of some organic compounds found in the HTC process water: acetic acid, benzene acetic acid, butanoic acid, pentanoic acid and propanoic acid were present in all their samples and they stated that these acids were produced from decomposition hydrolysis of the sludge. Alkenes, phenolic and aromatic compounds were also detected suggesting that hydrolysis, dehydration, decarboxylation, condensation, polymerisation, and aromatisation were occurred. Danso-Boateng et al. (2015b) reported also that several Maillard products such as aldehydes, furans, pyrroles, pyrazines, and pyridines were identified in liquid phase.

1.4.3 Gasseous Product

During HTC-process, a small amount of gas is released, 2-11 % weigh (Berge et al. 2011) and is mainly composed by CO_2 with traces of CO, CH_4, H_2 and NH_3 (Danso-Boateng et al. 2015b). The carbon present into the gaseous phase is mainly due to decarboxylation reactions, which are favoured by higher temperature (Funke and Ziegler 2010). In general, raising reaction temperatures lead to increases in gaseous yield consequence of the decrease of solid yield. Danso-Boateng et al. (2015b) found also hydrogen sulphide, nitrogen dioxide, nitric oxide, and ammonia in the gaseous phase. Hydrogen sulphide was probably produced as a result of Maillard reactions during the thermal decomposition of the sludge. Ammonia was also detected in all samples with other volatile hydrocarbons such as ethane. Berge et al. (2011) found also furans probably generated from the thermal decomposition of the cellulosic materials, condensation of aromatic compounds, and/or the thermal oxidation of lipids. Similar results were obtained by Fakkaew et al. (2018) and authors stated that to eliminate the toxic gases, odor and greenhouse gas emissions, the produced gases can be further treated with activated carbon adsorption or absorption with a wet scrubber. In the end Yoshikawa and Prawisudha (2014) performed odour tests with sewage sludge and hydrochar from the same feedstock. The main malodorous compounds in sewage sludge were sulphur compounds, such as hydrogen sulphide and methyl mercaptane, aldehydes, such as acetaldehyde, light aromatic compounds, such as styrene and toluene, and organic acids, such as propionic acid. After hy-

Table 1.6: literature review of HTC liquid characterisation associated with references of Table 1.4.

Feed.	**Temp. [°C]**	**Res. Time**	**TOC** $[gL^{-1}]$	**COD** $[gL^{-1}]$	**BOD** $[gL^{-1}]$	**VFA** $[gL^{-1}]$	$N-NH_4^+$ $[gL^{-1}]$	**pH** $[gL^{-1}]$	**Reference**
PSS	180	30-240 min	4.99-9.99	20.60-21.59	9.21-9.29	5.66-6.58	0.98-1.21	-	Danso-Boateng et al. (2015b)
	200	15-240 min	7.67-13.68	20.60-23.03	8.93-9.92	5.31-6.09	0.95-1.31	-	
	250	20 h	3	10	4	-	-	8	(Berge et al. 2011)
Dig.	220	30 min	4.58	12.99	-	0.41	1.7	7.1	(Aragón-Briceño et al. 2017)
	250	30 min	4.88	12.16	-	0.72	1.69	8.1	
US	180	60 min	-	12.75	-	-	-	-	(Xu and Jiang 2017)
	210	60 min	-	11.5	-	-	-	-	
	240	60 min	-	11	-	-	-	-	
	270	60 min	-	10	-	-	-	-	
FS	250	5 h	16.00–40.00	43.00–50.00	11.00–14.00	5.20–5.40	2	5.8–6.2	(Fakkaew et al. 2018)
Dig.	205	7 h	-	40.60–53.00	-	-	2.05–2.15	6.9–7.0	
DSS	190	5 h	-	37.53	-	-	1.37	5.1	(Escala et al. 2013)
	205	5-7 h	-	31.47–39.47	-	-	1.05–2.19	5.0–5.1	
	220	5 h	-	33.47	-	-	1.51	5	
Dig.	250	60 min	62.35	-	-	-	8.38	7.7	(Ekpo et al. 2016)

drothermal treatment, al sulphur compounds decreased, while aldehydes, light aromatic compounds and organic acids slightly increased involving decreasing discomfort due to malodorous.

1.5 Hydrochar Applications

Fang et al. (2018) gives a complete list of hydrochar potential application for different kind of feedstock. The main applications are: soil amendment in order to improve fertility and allow carbon sequestration; energetic applications, or as biofuels or as capacitor; low cost adsorbent by means of activation; sanitation and medical applications. In the following sections the applications of hydrochar produced from sludge are briefly summarised.

1.5.1 Energetic Applications

One of the main applications of HTC-coal is to use it as a combustible. The majority of the studies on hydrothermal carbonization were directed to recover energy from the waste biomass (Kim et al. 2014; Parshetti et al. 2013; Zhai et al. 2017). The HHV of hydrochar can be significantly increased compared to the original feedstock. On the other hand, HHV values of hydrochar produced from sludge hardly reach values above 20 – 21 $MJ\ kg^{-1}$ as reported in Table 1.4. Yoshikawa and Prawisudha (2014) stated that increasing reaction temperature, HHVs of hydrochar can slightly decrease due to dissolved solids that have significant calorific value. In order to overcome the problem, it is possible to use faecal sludge instead of water for other lignocellulosic biomass (Koottatep et al. 2016). However there are various options in which hydrochar can be used as a combustible: combustion plants, combined heat and power plants, cement and steel factories, mono-combustion plants for sewage sludge, gasification. Among other advantages, the HTC process permits also to obtain homogeneous hydrochar, suitable for co-combustion with coal (Zhai et al. 2017) leading also to lower SO_x and NO_x emissions due to the removal of N and S from sludge by means of HTC process (He et al. 2013; Peng et al. 2016). He et al. (2013) studied the combustion kinetics and found that hydrochar combustion could result in a more stable flame and a longer combustion process. Therefore, the produced hydrochar could be a significant substitute for natural coals in a typical combustion process. In developing countries, hydrochar can be used as cooking fuel in improved cooking stoves replacing firewood or charcoal derived from wood which could in consequence have a positive impact on deforestation. A novel scenario was proposed in Gai et al. (2016) where HTC is a pre-treatment combined with subsequent gasification: the steam

gasification of the hydrochar exhibited high hydrogen concentration and yield as well as high heating value, and gasification efficiency. In the end, Fakkaew et al. (2018) proposed an energy storage application: the hydrochar produced from faecal sludge could be processed further to make it suitable for use as an electrodes in batteries.

1.5.2 Sanitary and Medical Application

HTC in general sterilises the initial feedstock due to the high temperature and pressure, some authors have worked with microwave HTC in order to sterilise sludge (Afolabi et al. 2017), but hydrochar can also remove Escherichia coli (Fang et al. 2018). Fluorescent quantum dots produced from hydrochar are an emerging form of medical imaging for detection of disease at the cellular level (Fang et al. 2018). Another important application of HTC is the removal of pharmaceutical compounds (vom Eyser et al. 2015): most of the investigated compounds were removed or at least their concentrations reduced during the HTC process. Remaining residuals of pharmaceuticals in hydrochar after HTC were reported. Compared to sewage sludge, enhanced phenazone concentrations were detected in hydrochar. HTC process lead to high removal of Ibuprofen carbamazepine, bezafibrate, fenofibric acid, metoprolol, propranolol, clarithromycin, roxithromycin and erythromycin.

1.5.3 Soil Improvement

Another application of hydrochar is its use as water and ion binding component to improve soil quality (Libra et al. 2011). The use of hydrochar as a soil conditioner is reported to have positive effects on soil fertility and can be used for carbon sequestration (Libra et al. 2011; Danso-Boateng et al. 2015b). In general, Phosphorous precipitates at HTC conditions, and, typically, hydrochar from sewage sludge is rich of P, N, Na, K, Mg and Ca, providing many nutrients in order to improve soil fertility, although nutrient bioavailability is not well know yet (Aragón-Briceño et al. 2017; Escala et al. 2013; Sun et al. 2013). On the other hand, hydrochar from sludge can have high amount of heavy metals resulting toxic for human purposes. Hydrochar can also improves the nutrient retention capacity of the soil, which increases the nutrient supply for the plant and decreases the nutrient losses by leaching: first of all nutrients are bounded in the pores of hydrochar and secondly, slow biological oxidation produces carboxylic groups on the edges of the aromatic backbone of hydrochar which increases its nutrient holding capacity (Basso et al. 2013).

1.5.4 Adsorbent

One important application field for chars is adsorption, especially for water remediation. Hydrochars can be activated to increase their pore size and surface area. Thanks to their increased adsorption capacity, activated carbons can be used to adsorb a large variety of contaminants from water or soil. In general, the activation can be physical or chemical (Fang et al. 2018). Physical activation is carried out with activating agents such as CO_2 or steam at above 800 ℃. Chemical activation is carried out by mixing the hydrochar with chemical activating such as KOH or H_3PO_4 and heating the mixture at various temperatures in an inert environment (Fang et al. 2018). Fakkaew et al. (2018) measured BET surface area and total pore volume of dried initial faecal sludge and of the produced hydrochar: the authors stated that the HTC process enhances the BET surface area and the total pore volume of the produced hydrochar. The same authors found also mean pore diameters of the produced hydrochar (mesopores), meaning that hydrochar can adsorb large-sized molecules such as sugar and heavy metals, as well as small-sized molecules such as micropollutants. As a consequence, the produced hydrochar is a potential adsorbent for removing heavy metals and micropollutants from wastewater. The adsorption of Cu using the modified HTC as an absorbent was studied by Koottatep et al. (2017).

1.6 Energy Assessment

A promising application of HTC is for the treatment of sewage sludge from a waste water treatment plant (WWTP) but energy assessment are necessary. Escala et al. (2013) compared a scenario where sewage sludge is dried and incinerated in a combustion plant, with a scenario where the sewage sludge is hydrothermally carbonized, mechanically dewatered and then incinerated. The authors found that around 10 % of energy and up to 75 % of the cost for waste management can be saved per year with the application of HTC. Furthermore, it could improve the CO_2 balance by 95 %. Similar results were obtained by Zhai et al. (2017). Danso-Boateng et al. (2015a) conducted an energy balance of a semi-continuous HTC process of faecal waste conducted at 200 ℃ and at a reaction time of 30 min, based on recovering steam from the HTC process as well as energy from the solid fuel (hydrochar) and methane from digestion of the HTC liquid product. Results showed a positive energy balance for human faecal wastes with a solid content higher than 15-25%. In the end, in Zhao et al. (2014) is reported an energy balance for 1 ton / batch at 200 ℃ and 30 min showed in Figure 1.6. According to the energy balance, the energy recovery rate was around 40 % compared

with the standard sludge treatment (mechanical dewatering and thermal drying). In order to increase overall energy balance, also the configuration including the anaerobic digestion of sewage sludge, followed by the HTC of digestate and the anaerobic digestion of the HTC process water and hydrochar, must be considered. Aragón-Briceño et al. (2017) found that the overall energy produced for units of feedstock was 19.77, 18.88, and 17.96 $MJ\ kg^{-1}$ at HTC temperature of 160, 220, and 250 ℃, respectively coupling HTC of sludge with anaerobic digestion of HTC process water.

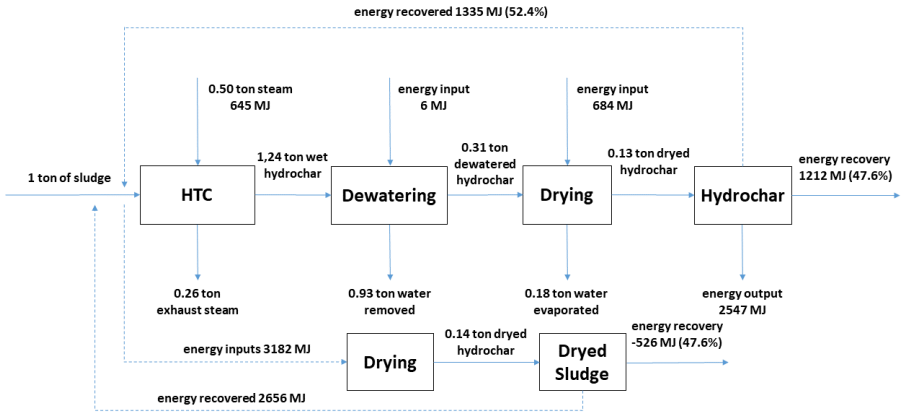

Figure 1.6: energy balance of hydrochar production by means of HTC (Zhao et al. 2014).

1.7 Conclusions

HTC of sewage sludge has great potential to become a sustainable conversion process for the management of sludge and the production of a wide variety of valuable products. In this review, the HTC implementation for sludge treatment has been analysed in terms of main operative parameters, products, applications and energy balance. HTC process temperature and residence time, initial sludge composition and concentration, nutrients concentration result as the main parameters, which influence the production of hydrochar by means of HTC process. Hydrochar can be exploited in different ways, mainly as a biofuel, as a soil improver and as potential adsorbent. Especially the adsorbent application need further studies since activated carbon has high costs and due to increasing pollution adsorbents are needed for water and soil remediation. HTC is a technology ready for full-scale implementation in a WWTP, but nowadays hydrochar hasn't its own legislation, so, at least in Italy, it is still considered a waste: further studies are needed in order to apply the circular economy concept and allow the conversion of hydrochar to a real

valuable and exploitable product.

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Chapter 2

Methane Production from Process Water of Hydrothermal Carbonisation of Sewage Sludge. A Review

This Chapter is a review on the anaerobic biodegradability of Hydrothermal Carbonisation process wastewater produced from the application of Hydrothermal Carbonisation of sewage sludge and other feedstocks. This chapter was submitted at *Critical Reviews in Environmental and Science Technology* journal on 22th February 2018, accepted with major revision and it is under review.

Methane Production from Process Water of Hydrothermal Carbonisation of Sewage Sludge. A Review

Valorising sludge through hydrothermal carbonisation

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2.0 Abstract

Hydrothermal carbonisation (HTC) has recently emerged as a promising technology for sustainable sludge minimization and solid products valorisation. Nevertheless, a not negligible amount of process water remains as by -product, containing organic compounds which solubilize during the process (10 – 63 $gCOD\ L^{-1}$). Its valorisation through anaerobic digestion (AD) has been assessed, but no systematic review has been reported to date. The main parameters, which influence the valorisation of HTC process water through AD, are initial feedstocks characteristics, nutrients concentration, HTC process temperature and residence time, inoculum acclimation to toxic compounds and its buffer capacity. Experiences reported in the literature proved that HTC applied to sewage sludge at 180 - 200 ℃ at residence times in the range 60 - 90 min could be a good compromise between hydrochar production and valorisation, hydrochar dewaterability, biogas production from AD of process water and energy consumption.

Keywords: Anaerobic digestion; Hydrothermal carbonisation; Process water; Sewage sludge.

2.1 Introduction

Conventional activated sludge (CAS) systems have been widely implemented to treat municipal wastewaters. CAS systems produce a significant amount of waste sludge, mainly composed of water and putrescible organic matter. Its subsequent treatment, which includes thickening, conditioning, dewatering, stabilisation, eventually drying and final disposal, represents up to 65 % of the operational costs of wastewater treatment plants (WWTPs) (Ferrentino et al. 2018). In Italy, the production of sludge reached about 1100 million kg (dry substance) in 2010 (EUROSTAT 2017) and this production will increase due to the construction of new WWTPs and the upgrading of existing ones because of more stringent effluent criteria. The main methods for waste sludge disposal in Italy are landfilling (48%), incineration (4%), composting (5%) as well as its reuse as soil conditioner in agriculture (33%) and other disposal sludge options (10%), involving severe environmental issues (EUROSTAT 2017; Lundin et al. 2004). Different technologies have been developed in order to minimize sludge production. Technologies integrated in wastewater handling units (known also as the water line) aim to reduce sludge production directly from biological treatments (Ferrentino et al. 2016). On the contrary, techniques integrated in the sludge handling units (known

also as the sludge line) have the objective to reuse sludge after its production for improving: *i)* biogas production in anaerobic digestion (AD) (Bougrier et al. 2006; Langone et al. 2015; Mancuso et al. 2017), *ii)* sludge dewaterability (Neyens and Baeyens 2003), and *iii)* resource recovery (i.e. nutrients, heavy metals, biofuels, biochar, hydrogen, syngas, biooil, biodiesel, proteins, bioplastics, biosorbents, etc.) (Tyagi and Lo 2013). Methods integrated in the sludge line are receiving increasing attention to pursue of a circular economy approach, like AD, incineration and co-incineration, gasification, pyrolysis, wet air oxidation, supercritical wet oxidation, hydrothermal liquefaction and hydrothermal carbonisation (Tyagi and Lo 2013). Among these processes, hydrothermal carbonisation (HTC) has emerged as a promising technology for efficient sludge minimization and relevant products valorisation (He et al. 2013). HTC process is realized by applying elevated temperatures (180 – 250 °C) to organic feedstock in suspension with water under saturated pressure for several hours, converting organic feedstock into a carbonaceous product (named char or hydrochar), which can be easily separated from the HTC process water later. Numerous studies focused on the characterization of hydrochar, which is biologically sterilized and exhibits a moderate calorific value, highly aromatic structures and mesoporous textures (He et al. 2013). Hydrochar can be used as a fuel for energy recovery, soil improver to increase soil quality, adsorbent or resource for phosphorous recycling and reclamation (He et al. 2013; Weber et al. 2014; Zhao et al. 2014). Recently, its valorisation through AD has been evaluated, too (Luz et al. 2018; Nilsson 2017)). However, large quantities of process water is obtained as by-product of HTC process; such water contains organic compounds which dissolve during the HTC process (Funke and Ziegler 2010; Stemann et al. 2013; Uddin et al. n.d.). HTC also produces a small amount of gas, which is mainly composed of CO_2 ($>$ 90 %) with minor amounts of CO and traces of H_2, CH_4 and light hydrocarbons (Basso et al. 2016). The carbon content of the gaseous phase represents only a minor loss during the HTC process, while the dissolved organic compounds in the HTC process water may contain more than 15 % of the initial feedstock energy (Stemann et al. 2013). Many researches focused on the characterization of HTC process water – often referred to also as HTC liquor (Danso-Boateng et al. 2015b; Ekpo et al. 2016b; Sun et al. 2013; Xu and Jiang 2017), while there are only few works on its utilization and valorisation. A possible application is represented by the HTC liquor recirculation to the HTC process (Stemann et al. 2013). However, the liquid recirculation to the HTC process is mainly feasible when solid biomasses with low humidity content are treated in the HTC process (Stemann et al. 2013). When sewage sludge is treated, the liquid recirculation to the HTC process is usually not required/possible, be-

cause of the high water content of sewage sludge, which depends on the type of sludge involved and the relevant dewatering system utilized in the WWTP (Metcalf&Eddy 2003). As a matter of fact, the liquor from HTC of sewage sludge represents a net output of the process and it has to be managed, treated and possibly valued. HTC process water valorisation through resource recovery is challenging (Ekpo et al. 2016a; Heilmann et al. 2016). Phosphorous recovery from the liquor from HTC of sewage sludge and the following organic fertilizer production have been industrially implemented (TerraNova© Ultra – Process). Nevertheless, the handling of HTC process water from sewage sludge inside the integrated WWTP-HTC system seems the best option in view of actual implementations: it's proved that the AD of HTC process water from sewage sludge can actually contribute to energetically sustain the HTC thermal energy requirements (Wirth et al. 2012; Wirth et al. 2015b). To the best knowledge of the authors, no systematic review has been reported to date on the valorisation of HTC process water from sewage sludge by means of AD. In the present review, the current state of the art on the AD of HTC process water is deeply discussed, emphasizing the importance of both HTC and AD operating parameters, as well as their possible limits. In addition, future directions for HTC research in this field are outlined.

2.2 Hydrothermal Carbonisation (HTC) of Sewage Sludge

HTC is an artificial coalification process that takes place in water. This thermochemical process converts inhomogeneous and wet biomass into hydrochar, a solid with characteristics intermediate between those of peat and coal, convertible in dry pellet. HTC occurs in liquid water at temperatures usually ranging from 180 ℃ to 250 ℃ (Basso et al. 2016), at the corresponding water vapour pressure (10 – 50 bar) and with typical residence times of 0.5 – 72 h (Funke and Ziegler 2010). HTC is able to convert carbohydrates into a carbonaceous residue referred to as hydrochar, which can be used for energy exploitation (Lucian et al. 2018b), as soil improver or adsorbent, or converted to other added value products (Parshetti et al. 2013; Yue et al. 2017; Purnomo et al. 2018). The HTC reaction path involves different steps: hydrolysis, dehydration, decarboxylation, condensation-polymerization and aromatization (Funke and Ziegler 2010; Libra et al. 2011; Lucian et al. 2018a; Volpe and Fiori 2017; Volpe et al. 2018). According to Funke and Ziegler (2010), these reactions are not consecutive, but can occur in parallel and their evolution depends on the initial feedstock characteristics; furthermore, the reaction pathway is not completely known and understood yet. In general,

the main reactions occurring during HTC are dehydration and decarboxylation Funke and Ziegler (2010), that have both negative enthalpy, so HTC is slightly exothermic (Funke and Ziegler 2011; Merzari et al. 2018). For this reason, the energy released progressively increases with stronger carbonisation and, correspondingly, the atomic ratios H/C and O/C decrease. Globally, de-oxygenation occurs: the oxygen is released in the form of carbon dioxide (CO_2) - decarboxylation - and water (H_2O) - dehydration. De-oxygenation is important because it reduces the polarity of the hydrochar surface, which consequently increases the dewaterability of the produced hydrochar. Hydrothermal carbonisation has been proposed as an interesting process to treat low value biomass, and among them sewage sludge, as a tool for CO_2 sequestration, considering that a significant fraction of carbon remains within the hydrochar during the HTC process (Titirici et al. 2007). Sewage sludge is the residue generated during the wastewater treatment processes. In general, its characteristics depend on the type of wastewater, the type of treatment and its operational strategies. Depending on the wastewater treatment stage in the wastewater handling units, sludge is categorized in *primary sludge* if produced during primary wastewater settling (physical and/or chemical); *secondary* or *waste activated sludge* (WAS), if produced during secondary biological treatments; *mixed sludge*, which is a primary and secondary sludge mixtures, and *tertiary sludge*, if produced during tertiary or advanced wastewater treatments. The produced sludge can be further processed in the sludge treatment-line, where it can be stabilized by means of digestion processes (digested sludge) and dewatered by means of solid/liquid separation systems (dewatered sludge). The composition of different sewage sludge differs in the percentage of carbon. Primary sludge has a higher organic carbon content than WAS and digested sludge (Metcalf&Eddy 2003). This can be explained by the conversion of organic compounds present in primary sludge into CO_2 and biogas, respectively in the biological processes in the water treatment line and in the AD process in the sludge treatment line. The chemical composition of sewage sludge is important when considering the final disposal of both the processed sludge (hydrochar) and the process water separated from the sludge during and after the HTC treatment (Li et al. 2015). In particular, the distribution of organic carbon, nutrients, heavy metals, pesticides, hydrocarbons between the HTC product streams affects the management of HTC final products. Table 2.1 provides chemical compositions and properties of different typologies of sludge, before the final drying – if any.

Interestingly, different kinds of sewage sludge, such as primary sludge (Danso-Boateng et al. 2015b), excess activated sludge (Wirth et al. 2015b) and municipal digested sludge (Aragón-Briceño et al. 2017; Huang and

Table 2.1: chemical composition and properties of untreated primary and secondary sludge and digested sludge (adapted from (Metcalf&Eddy 2003)).

Item / Sludge	Untreated primary sludge		Digested primary sludge		Untreated WAS
	Range	Typical	Range	Typical	Range
Total dry solids (TS), %	5 - 9	6	2 - 5	4	0.8 - 1.2
Volatile solids (% of TS)	60 - 80	65	30 - 60	40	59 - 88
Grease and fats (% of TS, ether soluble)	6 - 30	-	5 - 20	18	-
Grease and fats (% of TS, ether extract)	7 - 35	-	-	-	5 - 12
Protein (% of TS)	20 - 30	25	15 - 20	18	32 - 41
Organic matter (% TS)	47 – 70 [1]		43 – 64 [2]		63 – 82 [1]
Nitrogen (N, % of TS)	1.5 - 4	2.5	1.6 - 3.0	3.0	2.4 - 5.0
Phosphorous (P_2O_5, % of TS)	0.8 - 2.8	1.6	1.5 - 4.0	2.5	2.8 - 11
Potassium (K_2O, % of TS)	0 - 1	0.4	0 - 3.0	1.0	0.5 - 0.7
Cellulose (% of TS)	8 - 15	10	8 - 15	10	-
Iron (% of TS, not as sulphide)	2.0 - 4.0	2.5	3.0 - 8.0	4.0	-
Silica (SiO_2, % of TS)	15 - 20	-	10 - 20	-	-
pH	5.0 - 8.0	6.0	6.5 - 7.5	7.0	6.5 - 8.0
Alkalinity ($mgCaCO_3\ L^{-1}$)	500 - 1500	600	2500 - 3500	3000	580 - 1100
Organic acids ($mgHac\ L^{-1}$)	200 - 2000	500	100 - 600	200	1100 - 1700
Anti-inflammatory drugs *Ibuprofen* ($\mu g\ kgTS^{-1}$)	1425 – 2728 [3]	-	1020 -1262 [3]	-	524 – 3237 [3]
Antibiotics *Ibuprofen* ($\mu g\ kgTS^{-1}$)	< limit of detection [3]	-	< limit of detection [3]	-	< limit of detection [3]
Antiepileptic drug *Carbamazepine* ($\mu g\ kgTS^{-1}$)	0 – 66 [3]	-	18 – 28 [3]	-	231 – 460 [3]
Estrogens *17- Ethinylestradiol* ($\mu g\ kgTS^{-1}$)	28 – 53 [3]	-	20 – 70 [3]	-	24 – 160 [3]
Nervous stimulant *Caffeine* ($\mu g\ kgTS^{-1}$)	183 – 674 [3]	-	< limit of detection [1]	-	< limit of detection [3]
Cu ($mg\ kgTS^{-1}$)	80 – 120 [4]	-	204 – 337 [2]	-	74 -108 [4]
Cr($mg\ kgTS^{-1}$)	11 – 23 [4]	-	38 -3800 [2]	-	19 -45 [4]
Ni ($mg\ kgTS^{-1}$)	25 -49 [4]	-	17 -29 [2]	-	15 -47 [4]
Pb ($mg\ kgTS^{-1}$)	20 -36 [4]	-	58 -167 [2]	-	13 – 19 [4]
Mn ($mg\ kgTS^{-1}$)	55 – 111 [4]	-	- [3]	-	56 -90 [4]
Fe ($mg\ kgTS^{-1}$)	176 – 304 [4]	-	5000 -25000 [2]	-	300 -420 [4]
Cd ($mg\ kgTS^{-1}$)	0.6 – 1.4 [4]	-	1 – 18 [2]	-	0.6 – 1.4 [4]
Zn ($mg\ kgTS^{-1}$)	347 – 353 [4]	-	487 – 871 [2]	-	381 – 499 [4]
HHV ($MJ\ kg^{-1}$) *	23 - 29	25	9 - 14 [2]	12	19 - 23

References: [1] (Álvarez et al., 2002); [2] (Fuentes et al., 2004); [3] (Martín et al., 2012); [4] (Karvelas et al., 2003).
* HHV = Higher Heating Value.

Tang 2016), were investigated with different aims, helping to evaluate the possible implementation of the HTC treatment in a WWTP scheme. HTC of sewage sludge was studied by several authors for different purposes. As for other kinds of feedstock, most studies focused on the solid phase, the hydrochar, to convert sludge to a valuable product, improving its dewaterability (Escala et al. 2013; Bougrier et al. 2008). Many authors studied hydrochar, in order to exploit it for energy purposes as a renewable biofuel (Danso-Boateng et al. 2015b; He et al. 2013; Kim et al. 2014; Parshetti et al. 2013; Peng et al. 2016; Zhao et al. 2014), as well as renewable biomass for biogas production (Nilsson 2017), while other studies focused on other issues, such as the behaviour of nutrients (Ekpo et al. 2016b; Sun et al. 2013), pharmaceuticals (vom Eyser et al. 2015), and heavy metals (Zhai et al. 2016) in the products streams. Some authors focused on the use of hydrochar as adsorbent (Alatalo et al. 2013; Saetea and Tippayawong 2013) and soil improver (Breulmann et al. 2017; Danso-Boateng et al. 2012; Yue et al. 2017). Studies on HTC reaction kinetics were also conducted (Danso-Boateng et al. 2013). Danso-Boateng et al. (2015b) found that the higher heating value (HHV) of hydrochar from primary sludge could achieve values between 17.64 and 18.26 $MJ\ kg^{-1}$ when treating the sludge at 180 - 200 ℃ for 15 - 240 minutes. Nevertheless, the high moisture content could lead to a low thermal efficiency of HTC process, definable as the ratio between the HHV of dried hydrochar and the thermal energy required by the process, because a substantial amount of water per unit of mass of dry feedstock is treated (Lucian and Fiori 2017). Excess activated (or secondary) sludge has still a high moisture content and typically also a low carbon and high ash contents, so low HHV values then 15.82 $MJ\ kg^{-1}$ (HTC operating conditions: 250 ℃ and 15 min) have been reported (Parshetti et al. 2013). Aragón-Briceño et al. (2017) obtained a hydrochar with a HHV of 17.80 $MJ\ kg^{-1}$ treating digestate with 4.5 % solid content (TS) at 250 ℃ for 30 min. In Zhao et al. (2014) the HHV of hydrochar from dewatered sludge (14 % TS) achieved values of 20.17 $MJ\ kg^{-1}$ when performing HTC at 240 ℃ for 45 min. Notably, the solid content of the sludge to be fed to the HTC reactor can be increased by a pre-treatment dewatering step, which can substantially increase the thermal efficiency of HTC process. Finally, as HTC process of sewage sludge moved from laboratory to industrial scale, also studies on the liquid phase have been also carried out, in order to assess HTC process water valorisation by means of biodiesel or chemicals production (Xiao et al. 2012), biogas production (Ramke et al. 2009) and its recirculation to the HTC process (Stemann et al. 2013; Uddin et al. n.d.).

2.3 Characterization of HTC Process Water

HTC process waters contain high concentrations of organic matter as indicated by TOC, COD and BOD_5 concentrations and relatively abundance of soil nutrients (N, P, K). Tables 2.2 and 2.3 summarize the main findings reported in literature for HTC process waters from sewage sludge and biomasses, respectively. Generally, the chemical composition of HTC process waters is significantly affected by feedstock properties, feedstock load at the HTC reactor (usually expressed as dried inlet biomass (b) to initial total water (w) ratio) and HTC process conditions, mainly temperature and residence time (Wu et al. 2017) (Table 2.2). Regarding feedstock load, the total solid (TS) content in the feedstock can be substantially increased by dewatering/drying systems. Notably, Li et al. (2015) showed that the HTC process conditions significantly affect the carbon content in the HTC process water. In their study on sewage sludge, Danso-Boateng et al. (2015b) and Nyktari et al. (2017) proved that increasing HTC reaction temperature and time increased concentrations of organic compounds due to the hydrolysis of organic matter, as it resulted from increased concentrations of total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD). HTC process water from sewage sludge could contain up to 15 % of the initial carbon present in the sewage sludge, mainly as acetic acid (Wirth et al. 2015b). It's characterized by high TOC concentration (in the range of 3.7 - 62 $g\ L^{-1}$) and high COD concentration (in the range of 12.7 – 64 $g\ L^{-1}$) (Table 2.2). Aragón-Briceño et al. (2017) showed that the concentration of COD and TOC in the HTC process water from digestate increased 7-fold and 10-fold after HTC treatment, respectively. Higher COD concentrations were reported by Berge and Flora (2015), treating food waste, where the COD concentration reached 189 $g\ L^{-1}$, due to the initial feedstock kind and the high feedstock load used by the authors (Table 2.3). HTC process water from sewage sludge is characterized by a higher nutrient content than that resulting from the HTC of other biomasses. Aragón-Briceño et al. (2017) reported that total soluble phosphorus and nitrogen concentrations increased as the HTC temperature raised, while the concentration of reactive phosphorus decreased, probably due to precipitation reactions. Phosphorous tends to precipitate as solid phase during the HTC process and this tendency depends on carbonisation temperature (Ekpo et al. 2016b; Sun et al. 2013). Many organic compounds have been identified in the liquid phase from the HTC of sewage sludge, as reported by Danso-Boateng et al. (2015b). In the study of Nyktari et al. (2017), volatile fatty acids (VFAs) represent 9.8 – 30 % of TOC, depending on the HTC operating conditions. Among VFAs, acetic acid is known to reach the highest concentration and it pro-

vides the largest contribution to TOC: 6.2 % and 15 % in the cases of the studies of Wirth et al. (2015b) and Wirth and Reza (2016), respectively. A higher percentage has been measured, treating agricoltural biomasses. In the HTC process water from corn silage treatment, acetic acid was 33 % of TOC (Wirth and Mumme 2013), while it was in the range of 5 – 25 % in the HTC process water from orange pomace (Erdogan et al. 2015). Danso-Boateng et al. (2015b) proved that VFAs concentrations in HTC process water from sewage sludge decreased, as reaction temperature and reaction time increased from 140 to 200 ℃ and from 15 to 240 *min*, respectively. The authors explained this finding, as a result of further decomposition of organic acids into soluble products, such as furans (Goto et al. 2004; Sevilla and Fuertes 2009), as the reaction temperature and time increased. As a consequence of the presence of VFAs, HTC process water generally has a slight acid pH (Sevilla and Fuertes 2009). However, the pH value mainly depends on the treated feedstock and the HTC operating temperature (Ekpo et al. 2016b). Generally, HTC process water from primary and waste activated sludge has pH values lower than 6 (Table 2.2). On the contrary, Berge et al. (2011) found that process water from HTC of municipal anaerobic digested sludge remained slightly basic (about 8.0), as a consequence of the high buffering capacity of the feedstock used, which may hinder the initial hydrolysis step of HTC process. A similar result for digested sludge was obtained by Ekpo et al. (2016b) and Aragón-Briceño et al. (2017). Nyktari et al. (2017) showed the influence of HTC operating conditions on the pH: the higher the HTC processing temperature and treatment time, the lower pH value was achieved in the process waters, when treating sewage sludge. The carbonisation route follows hydrolysis, dehydration, decarboxylation, condensation, polymerisation and aromatisation (Funke and Ziegler 2010; Libra et al. 2011). This pathway was confirmed by Danso-Boateng et al. (2015b)) when treating primary sludge. The authors found organic compounds, like benzene, acetic acid, butanoic acid, pentanoic acid and propanoic acid, as products of the decomposition and hydrolysis of the sludge. Furthermore, they also detected alkenes, phenolic and aromatic compounds in all investigated HTC conditions, thus indicating the occurrence of dehydration of alcohols, condensation, polymerisation and aromatisation reactions. Danso-Boateng et al. (2015b) further reported the formation of toxic compounds when HTC was performed at temperatures higher than 180 - 200 ℃ and for reaction times longer than 15 *min*. In these conditions, several Maillard products such as aldehydes, furans, pyrroles, pyrazines and pyridines were identified in liquid samples, as consequence of the interactions between the proteins and carbohydrates present in the sludge, which may be difficult to treat (Miyata et al. 1996). As consequence of the Maillard (or caramel) reaction, HTC process water contains

dark brown coloured components. Moreover, the sulphur content in the liquid fractions from digestate has been showed to increase after the HTC treatment (Aragón-Briceño et al. 2017). Other compounds may be found in the HTC process water, depending on the feedstock properties. A few examples are presented here. Heavy metals may be found in the HTC water process (Erdogan et al. 2015). Treating lignocellulosic biomasses, phenols, furans, furfurals, 5-hydroxymethylfurfural (5-HMF) and other derivatives, originated from the decomposition of lignin, are usually detected in small concentrations in HTC process water (Berge et al. 2011; Funke and Ziegler 2010; Wang et al. 2012). High phenols concentrations in the process water from stabilized sewage sludge were also reported by Escala et al. (2013), with an average concentration 44 % higher for stabilized sludge , than for non-stabilized one. Acidic intermediates, such as lactic, formic and acetic acid, which are conversion products of sugars, have been detected treating orange pomace (Erdogan et al. 2015), while the HTC process water of brewer's spent grain included a multitude of fatty acids (mainly palmitic, oleic and linoleic acid), phenolic acids, short-chain mono- and di-carboxylic acids, alkylphenols, cyclic ketones, N- and S- functionalized organic compounds (Poerschmann et al. 2014).

2.4 Valorisation of HTC process water through anaerobic digestion and its challenges

The high organic content of HTC process water (10 - 64 $gCOD\ L^{-1}$) allows for its valorization through the AD process, which has been investigated by several research groups (Mumme et al. 2011; Poerschmann et al. 2014; Ramke et al. 2009; Wirth et al. 2015b; Oliveira et al. 2013). Concerning agricultural residues, several biomasses were first treated by HTC producing a HTC process water, that was fed to AD for energy valorisation, i.e. orange pomace (Erdogan et al. 2015), brewer's spent grain (Poerschmann et al. 2014), corn silage (Wirth and Mumme 2013), thin stillage (Wood et al. n.d.), seaweed (Smith and Ross 2016), food waste (Berge and Flora 2015), poultry manure, solid digestate, bedding material, a heterogeneous mixture mainly composed by hay, straw and manure and dry straw (Oliveira et al. 2013). In addition, industrial organic wastes, like cabbage and dough, and silvicultural residues, such as forest and landscape wood chips with low market value and forest wood chips with high market value, have been HTC treated and further the HTC process water has been valorised (Oliveira et al. 2013). Treating brewer's spent grain, Poerschmann et al. (2014) showed that the BOD_5/COD ratio of HTC process water (0.77 - 0.80) was significantly higher than that of the untreated feedstock (0.58), due to the

Table 2.2: chemical composition and properties of HTC process water from different kinds of sludge.

Feedstock	HTC conditions	TOC [g TOC L^{-1}]	COD [g COD L^{-1}]	VFAs [g L^{-1}]	Acetic Acid [g L^{-1}]	pH [-]	TS [%]	VS [% TS]	TAN [g N L^{-1}]	TKN [g N L^{-1}]	Phenols [mg L^{-1}]	Reference
Primary Sludge	180, 200 °C – 15, 30, 90, 120, 240 min	4.99 - 13.68	20.60 - 23.03	5.31 - 6.58	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.98 - 1.31	*n.d*	*n.d.*	(Danso-Boateng et al., 2015)
Sewage Sludge	200°C - 6h	13.4	34.3	*n.d.*	2.1	4.7	3.4	76.0	1.0	2.8	<3.1	(Wirth et al., 2015)
Sewage Sludge (HTC condensate)	200°C - 6h	3.7	12.7	*n.d.*	1.4	4.3	0.1	77.7	0.1	0.2	124.8	(Wirth and Reza, 2016)
Synthetic Sludge	180, 200°C – 30, 90, 120min	3.89 - 10.38	15.81 - 54.52	2.14 - 4.55	*n.d.*	4.41 - 5.06	1.88 -4.06	80.21 – 82.01	*n.d.*	*n.d.*	*n.d.*	(Nyktari et al., 2017)
Faecal Sludge (septic tank)	250°C – 5h	12 - 16	25 - 31	5.2 - 5.4	*n.d.*	5.8 - 6.2	*n.d.*	*n.d.*	*n.d.*	7 - 8	260	(Fakkaew et al., 2016)
Digestate from sewage sludge	250 °C - 1h	62.4	*n.d.*	*n.d.*	*n.d.*	7.7	*n.d.*	*n.d.*	*n.d.*	18.6	*n.d.*	(Ekpo et al., 2016)
Digestate from sewage sludge	220, 250 °C - 30 min	4.6 - 4.9	12.2 - 13.0	*n.d.*	0.4-0.7	7.1 - 8.1	*n.d.*	*n.d.*	*n.d.*	2.2 - 2.4	*n.d.*	(Aragón-briceño et al., 2017)
Digestate from sewage sludge	250 °C - 20h	4	10	*n.d.*	*n.d.*	8.0	*n.d.*	*n.d.*	*n.d.*	*n.d*	*n.d.*	(Berge et al., 2011)
Dewatered sludge	200, 220, 240 °C -20 min	24.1 - 21.3	63.9 - 50	*n.d.*	*n.d.*	8.6 - 8.2	*n.d.*	*n.d.*	*n.d.*	12 -11	*n.d.*	(He et al., 2015)
Dewatered sludge	190-221 °C - 5, 7 h	*n.d.*	31.5 - 53.0	*n.d.*	*n.d.*	5.0 - 7.0	*n.d.*	*n.d.*	*n.d.*	2.3 - 4.7	292 - 666	(Escala et al., 2013)
Dewatered sludge	180, 210, 240 °C -1 h	*n.d.*	10.0 - 12.8	*n.d.*	*n.d.*	< 6.8	*n.d.*	*n.d.*	*n.d.*	*n.d*	*n.d.*	(Xu and Jiang, 2017)

TOC = total organic carbon, COD = chemical oxygen demand, VFAs = volatile fatty acids, TS = total solid, VS = volatile solid, TAN = total ammonium nitrogen; TKN = total Kjeldahl *nitrogen*

Table 2.3: chemical composition and properties of HTC process water from a selection of different kinds of biomasses.

Feedstock	HTC conditions	TOC [g TOC L^{-1}]	COD [g COD L^{-1}]	VFAs [g L^{-1}]	Acetic Acid [g L^{-1}]	pH [-]	TS [%]	VS [% TS]	TAN [g N L^{-1}]	TKN [g N L^{-1}]	Phenols [mg L^{-1}]	Reference
Agricultural Residues	220°C – 4h	13 - 26	*n.d.*	*n.d.*	*n.d.*	3 - 5	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	(Oliveira et al., 2013)
Orange Pomace	190, 225, 260°C – 120 min	16 - 19	49 - 51	*n.d.*	3.1 - 3.7	3.90 - 4.64	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0 - 23.5	(Erdogan et al., 2015)
Brewer's Spent Grain	200, 240°C – 14h	14	60.8 - 64.2	*n.d.*	*n.d.*	2.8	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	(Poerschmann et al., 2014)
Corn Silage	200°C - 6h	15.66	41.35	*n.d.*	5.26	3.88	2.8	79.06	0.23	0.69	290	(Wirth and Mumme, 2013)
Thin Stillage	220°C – 1.25h	*n.d.*	50.13	*n.d.*	*n.d.*	4.82	4.02	83.58	*n.d.*	*n.d.*	*n.d.*	(Wood et al., 2013)
Food Waste + packaging	225, 250, 275°C – 0.5-96h	*n.d.*	58.2 - 189.0	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	(Berge and Flora, 2015)
Seaweed	200, 250°C – 1h	8.72 - 18.29	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	(Smith and Ross, 2016)

TOC = total organic carbon, COD = chemical oxygen demand, VFAs = volatile fatty acids, TS = total solid, VS = volatile solid, TAN = total ammonium nitrogen, TKN = total Kjeldahl nitrogen

breakdown of macromolecules, which suggests a good biological degradability. Danso-Boateng et al. (2015b) measured a BOD_5/COD ratio of 0.44 in the HTC process water of a primary sludge, which was suitable for AD process. AD is a biological conversion process where a complex microbial system converts organic compounds, in absence of oxygen, into biogas, that is mainly composed of methane and carbon dioxide (Batstone and Jensen 2011). A conversion of inorganic compounds can also occur, for example, sulphates can be converted into sulphur. AD performance depends on the coordinated activity of a complex microbial association, which is adequately dealt within the specialised literature (Metcalf&Eddy 2003; van Lier et al. 2008). Mainly, the substrate transformation by AD is composed by four successive stages as reported in Figure 2.1:

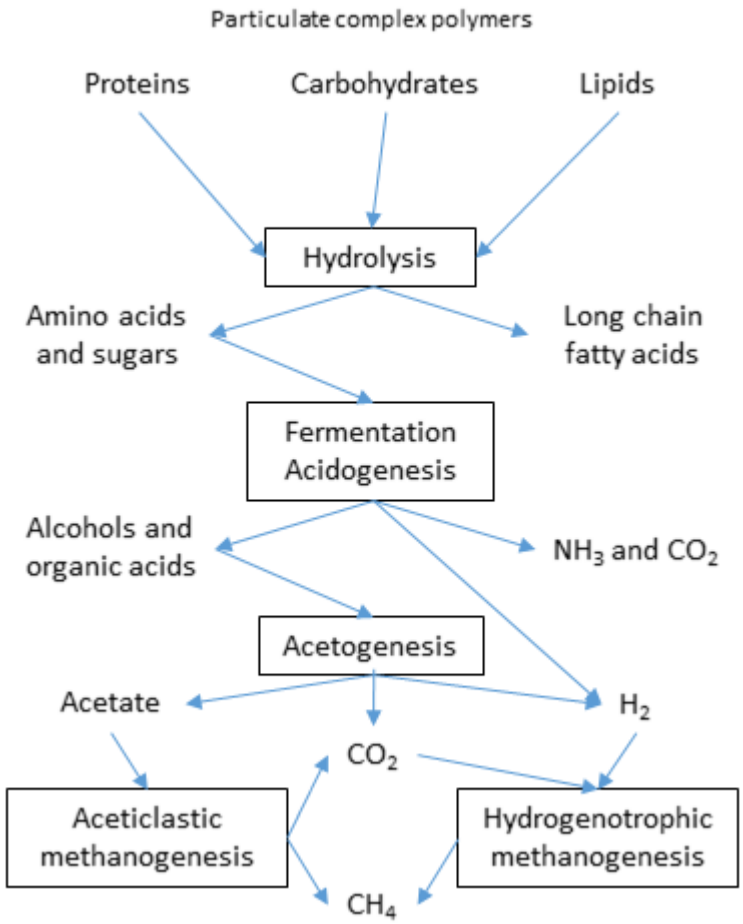

Figure 2.1: diagram of anaerobic digestion process (adapted from Batstone and Jensen (2011) and van Lier et al. (2008)).

1. Hydrolysis: it's an extracellular process where complex and particulate compounds (proteins, polysaccharides and fats) are solubilised by enzymes excreted by fermentative bacteria and typically is the rate limiting step;

2. Acidogenesis or fermentation: it's a process where soluble compounds are converted mainly into simple compounds, such as volatile fatty acids (VFAs), alcohols, CO_2, H_2, NH_3, H_2S, as well as new cell material;

3. Acetogenesis: it's the conversion of fermentation products into mainly acetic acid, CO_2 and H_2 as well as new cell material;

4. Methanogenesis: it's the final step, where methane is produced by two groups of methanogenic bacteria: the first group splits acetate into methane and CO_2 (aceticlastic methanogenesis), while the second group uses H_2 as electron donor and CO_2 as acceptor to produce methane (hydrogenotrophic methanogenesis).

Chemical composition of HTC process water is important, as the production of free fatty acid and nitrogen and the presence of some compounds can change or inhibit the AD microbial system. Macro- and micronutrients are generally present to a sufficient extent in sewage sludge HTC process water, satisfying the nutrient requirements of anaerobic bacteria (Wirth et al. 2015b). Nevertheless, according to Metcalf&Eddy (2003), the AD process is deeply influenced by pH levels, alkalinity, temperature and organic acid contents of the inlet feedstock. Lactic acid, acetic acid and glycerol present in HTC process water may negatively affect the fermentation process (Jacques et al. 1999). Additionally, the content of heavy metals, pesticides, VFAs, ammonia, Maillard compounds and toxic hydrocarbons needs also to be determined when HTC process water is treated through AD. Phenols, which are found in the HTC liquor due to the decomposition of furfural- like compounds (Sevilla and Fuertes 2009), may be also detrimental to AD process. Moreover, the sulphur content in HTC process water may have implications for levels of H_2S in the final biogas or for the precipitation of metal sulphides, when process water is sent to AD process (Aragón-Briceño et al. 2017). In the following sections, the influence on the AD process of potential inhibitory substances contained in HTC process water is discussed. Furthermore, the effects of inoculums acclimation, reactor configuration, temperature and organic loading rate (OLR) are analysed. Finally, biogas production from several HTC process water and its dependency on HTC operating conditions are reported, together with AD kinetics considerations.

2.4.1 AD Inhibitors

2.4.1.1 pH

The pH value is fundamental in the control of the AD process, since it has a direct effect on the enzymatic activity. Actually, each enzyme works in a certain pH range, but reaches its maximum activity at a well-defined, optimal pH. Hydrolysis is optimal above a pH of 6.0, acidogenesis between 5.5 and 8.0, acetogenesis between 6.5 and 8.0, and methanogenesis has its optimum at a pH between 7.0 and 8.0. In general, the AD is stable when pH is maintained around neutrality; an acceptable range of pH is between 5.5 and 8.0. Generally, pH values lower than the reported range indicate a VFAs accumulation in the AD reactor, likely caused by reactor overloading, which can lead to an inhibition of methanogenesis, if the system is poorly buffered. Higher pH values, instead, may lead to free ammonia accumulation (acid-basic pairs NH_4^+/NH_3 has pK_a level of 9.25), that can inhibit organisms growth (Batstone and Jensen 2011). Due to the slight acid pH of HTC process water from sewage sludge, dilution by recycling the AD effluent has been successfully used as a method to operate the AD process, providing optimum buffering and recycling nutrients (Nyktari et al. 2017). However, Wood et al. (n.d.) showed that AD of undiluted HTC process water from thin stillage with a pH of 4.7 can be carried out, when an inoculum with a sufficiently high alkalinity content (9803.3 $mgCaCO_3\ L^{-1}$) is used. Wirth and Mumme (2013), performing both anaerobic batch tests and continuous AD experiments on acidic process water from HTC of corn silage (pH = 3.88), showed that stable pH values of about 7.0 – 7.5 were achieved in the anaerobic reactors. A stable pH of 7.7 - 7.8 during anaerobic batch tests was also measured by Poerschmann et al. (2014), when treating process water from the HTC of brewer's spent grain (pH=2.8). Those results proved the general degradation capability of organic acids contained in HTC process water and the general feasibility of the AD treatment applied to HTC process water.

2.4.1.2 VFAs and Alkalinity

It's important to highlight that HTC process water has an initial high VFAs concentration (2.0 - 6.0 $g\ L^{-1}$), which increases as the HTC reaction temperature and reaction time decrease (Danso-Boateng et al. 2015b; Nyktari et al. 2017). On the one hand, Danso-Boateng et al. (2015b) showed that the higher the total VFAs concentration in the HTC process water, the higher was the methane yield achieved after feeding such liquor to AD. This is because VFAs, which are also produced by bacteria through acidogenesis during the second stage of AD, are further con-

verted to methane. On the other hand, alkalinity represents the ability of a system to neutralize the protons and it's generally expressed in terms of concentration of $CaCO_3$ in the liquid phase. Once alkalinity is consumed by the produced VFAs, the pH starts to drop, resulting in a higher concentration of non-dissociated VFAs, leading to methanogenic inhibition. Therefore, the buffering capacity of a system is essential in order to neutralize pH decreasing, when high VFAs concentrations are present in the AD system. For an anaerobic digester treating sewage sludge and operating in conditions of stability, the value of alkalinity is usually in the range 3000 - 5000 $mgCaCO_3\ L^{-1}$ (Graef and Andrews 1974). Usually, a stability index of AD is represented by the ratio of total VFAs to total alkalinity (TVFA/TA ratio), which can be interpreted as an acids-to-buffer ratio. In stable biogas plants, its value should be maintained below 0.4 to prevent over acidification (Zhao and Kugel 1996). Treating HTC process water from corn silage, a clear decline of the biogas production during continuous AD operation was observed by Wirth and Mumme (2013), together with an accumulation of VFAs and an increase of TVFA/TA ratio up to a value of 1.2.

2.4.1.3 Free Ammonia

Free ammonia (FA or $NH_3 - N$) and ammonium ($NH_4^+ - N$) concentrations in the HTC process water are the end-products of hydrolysis of proteins, urea and nucleic acids. Free ammonia in the AD process acts, at low concentrations, as substrate for bacterial growth (Yenigün and Demirel 2013) and contributes to the buffering capacity of the system, while at high concentrations (15 – 30 $mgNH_3 - N\ L^{-1}$) causes high pH and acts as inhibitor for anaerobic microbial activities (Batstone and Jensen 2011; Fagbohungbe et al. 2017). However, higher FA inhibition limits have been detected by Garuti et al. (2018a), Bujoczek et al. (2000), Angelidaki and Ahring (1994) and Lauterböck et al. (2012) whom observed anaerobic biological instability associated to ammonia inhibition at FA concentrations higher than 197, 250, 700 and 1000 $mg\ L^{-1}$, respectively. Free ammonia is in chemical equilibrium with its ionic form ($NH_4^+ - N$) and its concentration can be calculated as a function of pH, temperature and total ammonium nitrogen (TAN = $NH_3 - N + NH_4^+ - N$)(Wiesmann 1994). The formation of FA is favored at basic pH and at high temperature. AD inhibition by excess free ammonia usually occurs in digesters, where the feedstock has a high protein content. Wirth et al. (2015b) and Aragón-Briceño et al. (2017) stated that HTC process water from sewage sludge has enough nitrogen to allow bacterial growth in the AD process, while ammonia inhibition is unlikely.

2.4.1.4 Macro-Nutrients

Similar to other biological processes, both macro and micronutrients are required to maintain optimal microbial activity as well as AD performance. In HTC process water, phosphorous dissolved fraction decreases with HTC temperature (Ekpo et al. 2016b; Sun et al. 2013), thus at temperatures higher than 220 ℃ a lack of macronutrients may occur, due to phosphorous precipitation, when such HTC liquor is feed to AD. Anaerobically treating HTC process water from sewage sludge, Wirth and Mumme (2013) found that AD efficiency dropped after some weeks of operation, due to a lack of macronutrients in the HTC process water, especially phosphorous and sulphur, rather than nitrogen. This was explained considering that the studied HTC process water contained a relatively high ferrous iron concentration, which at neutral pH-values in the AD reactors starts to precipitate to form insoluble iron (II), sulphide (FeS) and iron (II) phosphate ($Fe_3(PO_4)_2$). Contrarily, in a following study, Wirth et al. (2015b) showed that N, S and P in the HTC process water of sewage sludge were available in sufficient concentrations of around 2000, 200 and 500 $mg\ L^{-1}$, respectively, throughout the AD experiment.Fakkaew et al. (2018) suggested adjusting the relative content of COD:N:P in the HTC process water from faecal sludge, in order to have them in the proportion 300:5:1. Nyktari et al. (2017) diluted HTC process water from sewage sludge ten times with the effluent from the AD reactor, both to avoid AD inhibition and to allow nutrient recycle.

2.4.1.5 Heavy Metals

Unlike other compounds, heavy metals are not biodegradable and accumulate over time until toxic concentrations are achieved. Heavy metals toxicity is linked to inactivation of a large number of enzymes. Inhibition phenomena depend on factors, such as the total concentration of heavy metals, their chemical form, pH, and redox potential (Thanh et al. 2016) . Concerning HTC process, heavy metals (such as copper, zinc, chromium, nickel, manganese, iron, as well as silicium, calcium and magnesium) tend to stay in the solid phase (hydrochar). Conversely, first group metals, like Na and K, are relatively water-soluble and can reach high concentrations in the liquid phase, in function of the kind of feedstock and operative conditions of HTC process (Poerschmann et al. 2014; Escala et al. 2013; Erdogan et al. 2015; Sun et al. 2013). However, many heavy metals are essential constituents of enzymes involved in bacterial activity (Fagbohungbe et al. 2017; Thanh et al. 2016). Besides basic macronutrients, micronutrients such as iron, copper, zinc, nickel, cobalt, manganese, potassium, calcium and molybdenum, at relatively low con-

centrations are necessary for supporting the metabolism of microorganisms in the AD process (Choong et al. 2016). Contrarily to the HTC process water from corn silage (Wirth and Mumme 2013), Wirth et al. (2015b) demonstrated that micronutrients present in the HTC process water from sewage sludge were present in sufficient concentration for the following AD process.

2.4.1.6 Toxic Organic Compounds

HTC process water may contain toxic organic compounds for AD microbial community, like phenols, furfurals and 5-HMF, produced, respectively, during de-structuring of lignin and dehydration reactions of pentose and hexose sugars (Fagbohungbe et al. 2017; Funke and Ziegler 2010; Libra et al. 2011; Wirth and Mumme 2013). Once formed in the HTC process, phenol is stable also at severe hydrothermal conditions (Castello et al. 2015). Phenol is a wastewater contaminant, low concentrations represent already an environmental risk for aquatic species and can cause taste and odour problems in drinking water; importantly, phenol can be recalcitrant during AD process due to its toxicity (Wirth et al. 2015a). Wirth et al. (2015a) stated that, with an appropriate inoculum adaptation, phenol can be degraded if the concentration is not too high. Over 99 % of phenol can be degraded during AD in thermophilic conditions, starting from wastewaters containing 630 $mg\ L^{-1}$ of phenol (Fang et al. 2006). Treating a synthetic solution, Wirth et al. (2015a)) found that phenol could be completely degraded up to 2000 $mg\ L^{-1}$ through AD under mesophilic conditions, using an adapted microbial community, but at 5000 $mg\ L^{-1}$ a complete inhibition occurred. Tables 2.2 and 2.3 report that phenol concentration in HTC process water can achieve concentration up to 700 $mg\ L^{-1}$, from which it can be supposed that HTC process water can be anaerobically treated after inoculum adaptation (Wirth et al. 2015a). Concerning furans, such as furfural and 5-HMF, Fagbohungbe et al. (2017) stated that these organic compounds are direct inhibitors for AD process, which can stand furans at a concentration lower than 25 mM. Other direct inhibitors of AD process are antibiotics and pesticides, which are present in industrial and pharmaceutical wastewaters (Ji et al. 2013; Lin 1990), as well as municipal sludge. While the residuals of pharmaceuticals in biochar from sewage sludge were investigated by vom Eyser et al. (2015), up to date the content in the HTC process water from sewage sludge requires to be analysed.

2.4.2 AD inoculum

As stated in the previous sections, AD to be stable needs enough nutrients, an alkalinity content function of VFAs concentration and a well-developed microbial community, capable of biodegrading phenols and other organic micro-pollutants. Several studies on the AD of HTC process water used as inoculum digestate from full-scale anaerobic digesters that process different feedstocks like grass, corn silage, manure (Berge and Flora 2015; Erdogan et al. 2015; Wirth et al. 2015b; Wirth and Mumme 2013; Wood et al. n.d.). In the lab-scale experiments reported in the scientific literature, the inoculum used for AD of HTC process water was either sieved and diluted to adjust total and volatile solids content (Wirth and Mumme 2013), or fed with nutrients solution, or buffered to adjust pH (Berge and Flora 2015), or gradually adapted to toxic organic compounds (Wirth et al. 2015b). In Berge and Flora (2015), methane yield was assessed in batch tests, using inoculums both acclimated and unacclimated to HTC process water. Using unacclimated inoculum, methane yield was 0.135 - 0.297 $L\ CH_4\ gCOD^{-1}$, depending on the different HTC conditions, while using acclimated inoculum methane yield increased to 0.218 - 0.427 $L\ CH_4\ gCOD^{-1}$. These results indicate that an acclimated microbial community could increase the tolerance to inhibitory compounds present in HTC process water. A methane yield of about 0.300 $L\ CH_4\ gCOD^{-1}$ was measured by Wood et al. (n.d.), anaerobically treating undiluted HTC process water from agricultural biomasses, using an unacclimated inoculum; however, a lag phase in methane production was observed from day 7 to day 12 of the batch assay. Similar results were achieved by Berge and Flora (2015), who further proved that acclimation of methanogens to HTC process water could shorten the lag phase. Concerning continuous AD experiments in literature, a start-up phase has been usually conducted before adding HTC process water, using a unique well-defined substrate. Wirth et al. (2015b) in their experiment fed the lab-scale AD reactor with microcrystalline cellulose, at an organic loading rate of 1.0 $gCOD\ L^{-1}\ d^{-1}$, twice within the first two weeks of operation. Wirth and Mumme (2013) used dextrose monohydrate at a loading rate of 0.5 $gVS\ L^{-1}\ d^{-1}$, further adding trace elements, while Berge and Flora (2015) used acetate at a loading rate of 0.3 $gCOD\ L^{-1}\ d^{-1}$ for the first 110 day of their AD reactor operation. Furthermore, Wirth et al. (2015b) showed that a gradual increase of the OLR from 1.0 to 5.0 $gCOD\ L^{-1}\ d^{-1}$ successfully adapted the anaerobic biomass to treat the HTC process water.

2.4.3 AD Reactors

Table 2.4 reports different reactor types used in research works that focus on AD of HTC process water. Mainly two AD reactor configurations have been applied to the treatment of HTC process water: continuous stirred tank reactors (CSTR) and anaerobic filters (AF). Over the entire test duration, the AF proved to be more stable, when treating HTC process water from corn silage, as confirmed by significantly lower levels of VFAs in the digestate and stable pH values (Wirth and Mumme 2013). Minor fluctuations in the gas production of the AF, compared to the CSTR, were also reported by the authors, probably favoured by immobilized microorganisms and sludge formation. AF has been successfully applied to treat HTC process water (Wirth et al. 2015b) and also HTC condensate (Wirth and Reza 2016) from sewage sludge. However, very few studies deal with continuous AD of HTC process water and, to the best of our knowledge, full-scale experiences with AD of HTC process water have not been reported yet. Considering the scarcity of the available literature on the topic, it's presently impossible to state which is the best AD reactor configuration and the relative operative conditions.

2.4.4 AD Temperature

Temperature influences the kinetics of biological processes. There are three different temperature ranges where AD can be performed, based on dominant microbial population: psychrophilic (10-30 °C), mesophilic (30-40 °C) and thermophilic (40-70 °C). From a biochemical point of view, it's generally accepted that temperature affects the reaction rate (in limited temperature ranges following the Arrhenius equation), the microbial activity causing inhibition after severe fluctuations, the microbial yields and the saturation concentrations, the reaction pathways due to free energy of reaction and the pathogen activity (van Lier et al. 2008). Temperature has also a direct effect on the physical and chemical properties of the components, such as the gas solubility, the volumetric gas production due to thermal expansion, the gas transfer rates, the water vapour fraction, the acid-base constants and the liquid viscosity (Batstone and Jensen 2011). HTC process water (Wirth et al. 2015b) and HTC condensate (Wirth and Reza 2016) from sewage sludge were anaerobically treated under both mesophilic (37 °C) and thermophilic (55 °C) conditions. In the thermophilic reactor, degradation of dissolved COD was always approximately 3.0 – 5.0 percentage points lower than values measured in mesophilic reactors, indicating a negative influence of increased digestion temperature in terms of performance. As a whole, mesophilic conditions are mostly applied. Nyktari et al. (2017) studied AD of HTC

Table 2.4: continuous anaerobic digesters utilized in literature concerning HTC process water.

Feedstock	AD reactor	Reactor volume	Operative Conditions	Efficiency	Reference
HTC process water from sewage sludge	Anaerobic Filter (AF)	30 L (working volume 26 L)	Bed carrier in PE 305m^2/m^3 Stirred with a recirculation pump OLR =1 – 5 gCOD $L^{-1}d^{-1}$ HRT = 5 – 34 d T= 37°C; 55°C	T= 37°C Biogas rate =0.191 – 0.927 L $L^{-1}d^{-1}$ Methane content = 74.8 – 76.6% COD removal efficiency = 75% T= 55°C Biogas rate =0.204 – 1.162 L $L^{-1}d^{-1}$ Methane content = 69.1 – 71.8% COD removal efficiency = 68%	(Wirth et al., 2015b)
HTC condensate from sewage sludge	Anaerobic Filter (AF)	30 L (working volume 26 L)	Bed carrier in PE 305m^2/m^3 Stirred with a recirculation pump OLR =0.8 gCOD $L^{-1}d^{-1}$ HRT = 16 d T= 37°C; 55°C	T= 37°C Biogas rate =0.232 L $L^{-1}d^{-1}$ Methane content = 75.4% COD removal efficiency = 69.8% T= 55°C Biogas rate = 0.240 L $L^{-1}d^{-1}$ Methane content = 68.6 % COD removal efficiency = 65.3%	(Wirth and Reza, 2016)
HTC process water from corn silage	Anaerobic Filter (AF)	3.8 L	450 plastic carriers 437m^2/m^3 Stirred with a recirculation pump OLR =1 g COD $L^{-1}d^{-1}$ HRT = 42 d T= 37°C	Biogas rate =0.25 – 0.30 L $L^{-1}d^{-1}$ Methane content = 66 – 67% COD removal efficiency = 61.4 -69.4%	(Wirth and Mumme, 2013)
HTC process water from sewage sludge	Fixed Film Anaerobic Digester	9 L	Dilution by recycling digestate (dilution ratio of 10:1) OLR =2 - 5 gCOD $L^{-1}d^{-1}$ HRT = 1.8d; 0.9 d T= 37°C	Biogas rate =0.08 – 0.977L $L^{-1}d^{-1}$ Methane content = 66 – 67% COD removal efficiency = 58 - 88%	(Nyktari et al., 2017)
HTC process water from corn Silage	Continuous Stirred Tank Reactor (CSTR)	3.8 L	450 plastic carriers 437m^2/m^3 Stirred OLR =1 g COD $L^{-1}d^{-1}$ HRT = 42 d T= 38°C	Biogas rate =0.25 – 0.37 L $L^{-1}d^{-1}$ Methane content = 60% COD removal efficiency = 60.7 -74.9%	(Wirth and Mumme, 2013)

process water from synthetic primary sludge at mesophilic condition (37 ℃), while Aragón-Briceño et al. (2017) performed bio-methane potential (BMP) tests at 37 ℃ on the HTC process water from digested sludge. Pinnekamp (1989) assessed methane production at 33 and 55 ℃ after hydrothermal treatment of sludge in the range 100 – 220 ℃, without separation between solid and liquid phases. Also referring to other kinds of waste biomass, AD of HTC process water under mesophilic conditions is the most studied process:

- agricultural residues at 38 ± 2 ℃(Oliveira et al. 2013);
- orange pomace at 42 ± 2 ℃(Erdogan et al. 2015);
- brewer's spent grains at 38 ℃(Poerschmann et al. 2014);
- corn silage at 37 ℃(Wirth and Mumme 2013);
- thin stillage at 37 ℃(Wood et al. n.d.);
- food waste at 38 ℃(Berge and Flora 2015);
- phenol-polluted wastewaters at 37 ℃(Wirth et al. 2015a).

2.4.5 AD Organic Loading Rate (OLR)

The organic loading rate is a crucial operative parameter of the AD process: an overload can lead to VFAs accumulation and consequently to the inhibition of the methanogenesis process. The OLR is also a function of the technology chosen: high rate anaerobic digesters, such as AF, can reach OLR up to 20 $gCOD\ L^{-1}\ d^{-1}$, while other reactors such as CSTR can reach OLR up to 10 $gCOD\ L^{-1}\ d^{-1}$ (Batstone and Jensen 2011). Concerning AD of HTC process water from sewage sludge, the influence of OLR on two continuous AD reactors in mesophilic and thermophilic conditions was studied by Wirth et al. (2015b). The authors found that both reactors adapted very fast to increased OLRs (from 1 to 5 $gCOD\ L^{-1}\ d^{-1}$) and shortened hydraulic retention time (HRT, from 34 to 5 days). COD removal efficiencies and methane yields were not affected by shorter HRTs, reaching an almost constant methane yield of 0.18 $L\ CH_4\ gCOD^{-1}_{added}$. In Berge and Flora (2015), instead, with an OLR equal to 0.3 $gCOD\ L^{-1}\ d^{-1}$ and HRT of 10 days, unstable AD was reported, probably due to a not well-acclimated biomass.

2.4.6 Biogas Production from HTC Process Water

In Table 2.5 and 2.6, a summary of literature results concerning AD performances when treating HTC process water from different sludge and

biomasses is reported, respectively. The main indicators are represented by the methane and the biogas yields, as a function of HTC process conditions and AD parameters such as OLR and HRT. If available, also COD removal efficiency data are reported.

2.4.6.1 Bio-Methane Potential (BMP) Tests and Methane Yield

Bio-Methane Potential (BMP) tests represent a useful batch tool to measure the biogas production from organic waste (Esposito et al. 2012) and are commonly used in studies concerning the AD of HTC process water (Aragón-Briceño et al. 2017; Berge and Flora 2015; Erdogan et al. 2015; Wood et al. n.d.). BMP tests are performed under controlled and reproducible conditions, usually in 100 – 2000 mL glass bottles, filled with substrate (S) and inoculum (I) at mesophilic or thermophilic conditions, using a S/I ratio in the range 0.5 – 2.3 $gVSgVS^{-1}$ to prevent acidification phenomena (Neves et al. 2004). Micronutrients may be added as trace elements. A BMP test using only the inoculum (blank) is also performed to determine the background effect of the inoculum. The experimental duration of a BMP test is 21 - 30 days, during which the biogas and/or methane volume produced is monitored. To compare biogas production results, the volume of biogas measured at ambient conditions in the batch test has to be firstly converted to the volume at standard conditions using the ideal gas law 2.4.1 (VDI4630 2006):

$$V_{STP,HTC} = V_{HTC} \frac{(p_{test} - p_{w,test})}{p_0} \frac{T_0}{T_{test}} \tag{2.4.1}$$

where $V_{STP,HTC}$ is the standard volume of biogas from the HTC process water (mL), V_{HTC} is the biogas volume measured in the BMP bottle (mL), p_{test} and T_{test} are, respectively, the pressure ant the temperature of the BMP bottle, $p_{w,test}$ is the water vapour pressure computed at T_{test} and, finally, p_0 and T_0 are, respectively, the standard pressure and temperature (p_0=1.01325 bar, T_0=273.15 K). Then, in order to consider BMP tests performed in different reactor types and at different loading rates, the specific volumes of biogas and methane are calculated, usually using COD, TOC or VS as the basis. The total biogas yield (Y_{biogas}, expressed in $mL\ biogas\ gCOD^{-1}_{added}$) and the methane yield (Y_{CH4}, expressed in $mL\ CH_4\ gCOD^{-1}_{added}$) are generally computed respectively by using equations 2.4.2 and 2.4.3:

$$Y_{biogas} = \frac{V_{STP,HTC}}{C_0} \tag{2.4.2}$$

$$Y_{CH_4} = \frac{V_{STP,HTC}}{C_0} \times \%_{CH_4} \tag{2.4.3}$$

Table 2.5: summary of literature results concerning the valorisation of HTC process water from different kinds of sludge.

HTC Feedstock	HTC reaction temperature	HTC reaction time	HTC b/w	AD Conditions	Biogas Yield	Methane Yield	Methane fraction	COD conversion	Note	Reference
Primary Sludge	180 °C 200 °C	60 min 15 min 30 min	0.045	Modelling	-	-	44.9-62.5% 44.5-50.7% 44.2-51.6%	-	Separation via vacuum filtration, 10µm pores	(Danso-Boateng et al., 2015b)
Sewage Sludge	200 °C	6 h	-	T= 37 °C T= 55 °C Long – term experiments: OLR = 1- 5 gCOD L^{-1} d^{-1} No micro and micronutrients added No VFA accumulation	-	0.144-0.178 L CH_4 $gCOD^{-1}$ 0.147-0.170 L CH_4 $gCOD^{-1}$	75-77% 69-72%	68% 75%	40kg of citric acid added as additive to 754kg of sludge; separation with filter press	(Wirth et al., 2015b)
Sewage Sludge (HTC condensate)	200 °C	6 h	-	T= 37 °C T= 55 °C Long – term experiments: OLR = 0.8 gCOD L^{-1} d^{-1} Micro and micronutrients added	-	0.022-0.220 L CH_4 $gCOD^{-1}$ 0.024-0.211 L CH_4 $gCOD^{-1}$	75-84% 56-76%	7-70% 7-67%	-	(Wirth and Reza, 2016)
Synthetic Sludge	180 °C 200 °C	30 min 90 min 120 min 30 min	0.11	Long – term experiments: T= 37 °C OLR = 1.8- 3.6 gCOD L^{-1} d^{-1} biogas rate 0.08-0.51L L^{-1} d^{-1}	-	0.106 L CH_4 $gCOD^{-1}$ 0.093 L CH_4 $gCOD^{-1}$ 0.209 L CH_4 $gCOD^{-1}$ 0.026 L CH_4 $gCOD^{-1}$	-	76% 78% 40% 62%	Separation with a 60 micron stainless steel filter	(Nyktari et al., 2017)
Faecal Sludge (septic tank)	250 °C	5 h	0.25	Batch experiments	-	0.003 L CH_4 $gCOD^{-1}$ 0.002 L CH_4 gFS^{-1}	-	-	Separation via vacuum filtration through a 1.2 µm filter	(Fakkaew et al., 2018)
Digestate	220 °C 250° C 220 °C 250° C 220 °C 250° C	30min 30min 30min	0.045	Batch experiments: T= 37°C Buswell's equation (model) Boyle's equation (model)	-	0.277 L CH_4 $gCOD^{-1}$ 0.226 L CH_4 $gCOD^{-1}$ 0.384 L CH_4 $gCOD^{-1}$ 0.513 L CH_4 $gCOD^{-1}$ 0.289 L CH_4 $gCOD^{-1}$ 0.403 L CH_4 $gCOD^{-1}$	-	80% 64%	The authors performed BMP test on both slurry and HTC liquor, here are reported only data concerning HTC liquor.	(Aragón-briceño et al., 2017)
Excess, Digested and Primary Sludge	180-220°C	45-150min	-	T = 33 °C and 55 °C HRT 20 d HRT 10 d HRT 7.5 d	0.190-0.600 L gVS^{-1} 0.190-0.400 L gVS^{-1} 0.200-0.350 L gVS^{-1}	-	-	-	AD performed on the slurry and not on HTC liquor	(Pinnekamp, 1989)

Table 2.6: summary of literature results concerning the valorisation of HTC process water from different kinds of biomass.

HTC Feedstock	HTC reaction temperature	HTC reaction time	HTC b/w	AD Conditions	Biogas Yield	Methane Yield	Methane fraction	COD conversion	Note	Reference
Corn silage	220 °C	6 h	-	CSTR Anaerobic Filter Long – term experiments: OLR = 1 gCOD L^{-1} d^{-1} HRT 42d	-	0.163-0.624 L CH_4 $gCOD^{-1}$ 0.178-0.577 L CH_4 $gCOD^{-1}$	60-65%	52-75% 56-69%	-	(Wirth and Mumme, 2013)
Agricultural Residues	220 °C	4 h	0.176	Batch experiments: T= 37°C	0.0096-0.0211 L gFM^{-1}	0.006-0.0163 L CH_4 gFM^{-1}	63-77%	-	-	(Oliveira et al., 2013)
Orange Pomace	190 °C 225 °C 260 °C	120 min	0.125	Batch experiments: T= 42°C	0.337 L $gCOD^{-1}$ 0.324 L $gCOD^{-1}$ 0.296 L $gCOD^{-1}$	0.214 L CH_4 $gCOD^{-1}$ 0.209 L CH_4 $gCOD^{-1}$ 0.195 L CH_4 $gCOD^{-1}$	63% 65% 66%	-	-	(Erdogan et al., 2015)
Brewer's Spent Grain	200 °C 240 °C	14 h	0.133	Batch experiments: T= 38°C	0.479 L $gODM^{-1}$ 0.654 L $gODM^{-1}$	0.287 L CH_4 $gCOD^{-1}$ 0.405L CH_4 $gCOD^{-1}$	60% 62%	-	80µg/mL of citric acid added as catalyst; separation with filter paper	(Poerschmann et al., 2014)
Thin Stillage	220 °C	1.25 h	0.072	Batch experiments: T= 37°C	-	0.270-0.300 L CH_4 $gCOD^{-1}$	-	91-92%	-	(Wood et al., 2013)
Food Waste + packaging	225 °C, 250 °C, 275 °C	0.5-96 h	0.32	Batch -Unacclimated organisms -Acclimated organisms	-	0.135-0.297 L CH_4 $gCOD^{-1}$ 0.218-0.427 L CH_4 $gCOD^{-1}$	-	39-85% 60 - 120%	Separation via vacuum filtration through a 0.45 µm filter	(Berge and Flora, 2015)
Seaweed	200 °C 250 °C	1 h	0.1	Model	-	60.1-96.0 g CH_4 $kgODM^{-1}$ 52.7-102.5 g CH_4 $kgODM^{-1}$	-	-	Separation with vacuum filtration using 110 mm filter paper	(Smith and Ross, 2016)

where $V_{STP,HTC}$ is the standard biogas volume (mL) produced in bottle from the HTC process water, C_0 is the mass of substrate added to the system, in terms of grams of COD, TOC or VS and $\%_{CH_4}$ is the volumetric fraction of methane (Erdogan et al. 2015). The cumulative methane production data from the experiments can be modelled using different models, such as the first order equation 2.4.4 (Banu et al. 2018c; Banu et al. 2018a; Ushani et al. 2018):

$$M_p = M \times \left(1 - e^{-k \times t}\right) \tag{2.4.4}$$

where M_p is the cumulative methane production ($gCOD\ gCOD^{-1}$), M is the methane production potential ($gCOD\ gCOD^{-1}$), k is the disintegration rate constant (d^{-1}) and t is time (d). The modified Gompertz equation (Kavitha et al. 2014; Kavitha et al. 2018; Banu et al. 2018b) is another model for the cumulative biogas production expressed in equation 2.4.5:

$$B_t = B \exp\left(-\exp\left(\frac{R_b}{B}\exp\left(\lambda - t\right) + 1\right)\right) \tag{2.4.5}$$

where B_t is the cumulative biogas produced ($L\ gVS^{-1}$) at time (t), B is the biogas production potential ($L\ gVS^{-1}$), R_b is the maximum biogas production rate ($L\ gVS^{-1}\ d^{-1}$) and λ is the lag phase (d), which is the time required for bacteria to acclimatize; B, R_b and λ are constants determinable using non-linear regression methods. In the end, a combination of first order equation and modified Gompertz equation were was also proposed as expressed in equation 2.4.6 (Bolado-Rodríguez et al. 2016; Garuti et al. 2018b).

$$B_t = B_{01}\left(1 - e^{-k\ t}\right) + B_{02}\exp\left(-\exp\left(\frac{R_b}{B_{02}}\exp\left(\lambda - t\right) + 1\right)\right) \tag{2.4.6}$$

where B_{01} is the methane potential from microorganisms able to grow in the inhibitory environment (first order kinetic) and B_{02} is the methane potential from microorganisms able to acclimate in the pre-treatment medium. The methane yields (Y_{CH_4}) from HTC process water of organic waste ranged between 0.022 - 0.427 $L\ CH_4\ gCOD^{-1}$). CH_4 yields of process water from HTC of orange pomace was in the range of 0.196 to 0.213 $L\ CH_4\ gCOD^{-1}_{added}$). Similar yields were reported for AD of liquors from HTC of corn silage (Wirth and Mumme 2013) and several agricultural residues (Oliveira et al. 2013). The methane yield of HTC process water from different kinds of sludge was lower, between 0.022 - 0.277 $L\ CH_4\ gCOD^{-1}$ in the HTC temperature range of 180 – 250 ℃ and residence time of 0.5 – 6 h. Aragón-Briceño et al. (2017) found that the

methane production from HTC process water from digested sludge was 1.29 - 1.58 times the biogas production from filtered digestate (control liquor), working at HTC process conditions of 220 - 250 ℃ for 30 min. Similar results were found out by Qiao et al. (2011).

2.4.6.2 Theoretical BMP (BMPth)

The calculation of theoretical BMP values (BMP_{th}) is usually reported in literature for HTC process water to easily determine the methane productivity from substrate elemental composition, COD characterization, or organic fraction composition (Nielfa et al. 2015). To estimate the theoretical methane yield (expressed as $L\ CH_4\ gVS^{-1}$) by methanogenesis of HTC process water from sewage sludge, Danso-Boateng et al. (2015b) used the Buswell's equation (Buswell and Neave 1930) (Eq. 2.4.7), by taking into account the elements C, O and H in the dried carbonized solid to mimic HTC process water composition 2.4.8.

$$\begin{aligned} &C_nH_aO_b + \left(n - \tfrac{a}{4} - \tfrac{b}{2}\right) H_2O \rightarrow \\ &\rightarrow \left(\tfrac{n}{2} + \tfrac{a}{8} - \tfrac{b}{4}\right) CH_4 + \left(\tfrac{n}{2} - \tfrac{a}{8} + \tfrac{b}{4}\right) CO_2 \end{aligned} \tag{2.4.7}$$

$$Y_{th,BW}\left[\frac{mL\ CH_4}{gVS}\right] = \frac{22400\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)}{12n + a + 16b} \tag{2.4.8}$$

where $C_nH_aO_b$ represents, in this case, the chemical formula of the carbonised solids while n, a and b are the amount of C, H and O, respectively, in the carbonised sludge. Further, the molar percentage of CH_4 in the biogas has been calculated according to Eq.2.4.9

$$\%CH_{4,BW} = \frac{\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)}{\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right) + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)} \times 100 \tag{2.4.9}$$

The presence of proteins and ammonia in the HTC process water has been considered by Smith and Ross (2016), who applied the Boyle's equation (Raposo et al. 2011) (Eq. 2.4.10) to compute the theoretical methane yield via methanogenesis, expressed as g$g\ CH_4\ gVS^{-1}$ or $L\ CH_4\ gVS^{-1}$, from the elementary composition of the dried HTC process water resulting from seaweed (Eq. 2.4.11).

$$\begin{aligned} &C_nH_aO_bN_c + \tfrac{(4n-a-2b+3c)}{4} H_2O \rightarrow \\ &\rightarrow \tfrac{(4n-a+2b+3c)}{8} CO_2 + \tfrac{(4n+a-2b-3c)}{8} CH_4 + 3cNH_3 \end{aligned} \tag{2.4.10}$$

$$BMP_{th,BO}\left[\frac{mL\ CH_4}{gVS}\right] = \frac{22400\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)}{12n + a + 16b + 14c} \tag{2.4.11}$$

where $C_nH_aO_bN_c$ represents the chemical formula of HTC process water samples dried at 60 ℃ over a period of 48 h, while n, a, b and c are the amount of C, H, O and N respectively in the dried HTC process water samples. In Aragón-Briceño et al. (2017) both Buswell's equation and Boyle's equation were applied and compared with experimental methane production results, to define how accurate those equations are in order to determine the methane yield from HTC process water from sewage sludge. In their study, the used chemical formula represents the HTC process water samples. The authors found that Y_{th} values in both cases were higher than the experimental values. The Boyle's equation had the closest match to the experimental values and that may be due to the fact that the model considers the presence of nitrogen, proteins and ammonia. Danso-Boateng et al. (2015b) further calculated the molar percentage of CH_4 in the biogas from the amount of COD and TOC concentration in the HTC process water from sewage sludge, according to a correlation proposed by Franco et al. (2007) (Eq. 2.4.12).

$$\%CH_{4,COD} = \left[0.5 - \frac{4 - 1.5\left(\frac{COD_{HTC}}{TOC_{HTC}}\right)}{8}\right] \times 100 \qquad (2.4.12)$$

Franco's correlation furnished higher molar percentage of CH_4 in the biogas as compared to the results obtained using the Buswell's equation (Danso-Boateng et al. 2015b). Interestingly, Smith and Ross (2016) proposed a model to calculate the hydrogen production via hydrogenesis by AD of seaweed HTC liquor, expressed as $gH_2\ gVS^{-1}$ or $L\ H_2\ gVS^{-1}$, by taking into account the elements C, H and O in the dried HTC process water (Eq. 2.4.13).

$$C_xH_yO_z + (2x - z)\,H_2O \rightarrow \left(\frac{y}{2} + (2x - z)\right)H_2 + xCO_2 \qquad (2.4.13)$$

where $C_xH_yO_z$ represents the chemical formula of HTC process water samples dried at 60 ℃ over a period of 48 h, while x, y and z are the amount of C, H and O, respectively, in the dried HTC process water samples.

2.4.6.3 AD Performance as a Function of HTC Process Conditions

Methane yield is affected by many parameters, among them initial feedstock and relative biomass to water (b/w) ratio and HTC process conditions, as showed in Tables 2.5 and 2.6. This result is evident with the fact that those variables first affect the chemical composition of HTC process

waters (Tables 2.2 and 2.3) (Li et al. 2015). Concerning the HTC process conditions, the CH_4 yields of liquor from HTC of orange pomace slightly decreased from 0.213 to 0.196 $L\ CH_4\ gCOD_{added}^{-1}$ when increasing the HTC temperature (from 190 to 260 °C for 120 min). Similar results were reported for AD of liquor from HTC of sewage sludge (Danso-Boateng et al. 2015b). The authors showed that the molar percentage of CH_4 in the biogas from HTC liquor from sewage sludge was significantly affected by HTC conditions and decreased as HTC temperature and time increased. The authors also found a mathematical model to describe the influence of HTC parameters - reaction temperature, T (°C) and reaction time, t_R (min) - on the AD performances, as showed in the following equations (Eq.s 2.4.14, 2.4.15):

$$CH_{4,BW}\,[\%] = 45.40 - 1.38T - 1.12t_R + 0.93Tt_R \tag{2.4.14}$$

$$CH_{4,COD}\,[\%] = 118.11 - 0.66T - 0.21t_R + 4.55 \cdot\ 10^{-4}Tt_R \tag{2.4.15}$$

The predicted results obtained from the model equations were close to the experimental results having standard errors ranging between 0.52 – 3.44 % for methane yield from Buswell's equation (R^2 = 0.64) (Eq. 2.4.14) and 0.12 – 20.11 % (R^2 = 0.83) for methane yield using the correlation of Franco et al. (2007) (Eq. 2.4.15).

2.4.6.4 Kinetics Considerations

For the AD of HTC process water both hydrolysis and methanogenesis constants have been determined, proving that hydrolysis can be identified as a very fast process, while methanogenesis seems to be the most probable rate-limiting phase in AD of HTC liquor (Wirth et al. 2015b; Wirth and Reza 2016). This can be explained considering the absence of complex organic compounds in the HTC liquor and the presence of inhibitory compounds (Batstone and Jensen 2011; Wirth and Mumme 2013). According to Pohl et al. (2013), Wirth et al. (2015b) calculated the hydrolysis constant, k_H, by a weekly COD balance for several OLRs applied to their continuous AD reactor (Eq. 2.4.16). At an OLR of 1 $gCOD\ L^{-1}\ d^{-1}$, the k_H was calculated to be 0.989 ± 0.013 d^{-1} and 0.979 ± 0.013 d^{-1} in the mesophilic and thermophilic system, respectively. Further, the k_H values slightly decreased at increasing OLR. This can be explained by shortened HRTs. Comparing these values with k_H values determined for the digestion of more complex organic waste, i.e. wheat straw, it can be stated that hydrolysis in anaerobic HTC liquor digestion is a very fast process. Similar values of 0.993 ± 0.005 d^{-1} and 0.993 ± 0.003 d^{-1} were found for the mesophilic and thermophilic system

for treating the HTC condensate from sewage sludge (Wirth and Reza 2016).

$$k_H = 1 - \frac{COD_{degraded} + COD_{digestate} - COD_{substrate}}{COD_{reactor}} \quad (2.4.16)$$

where $COD_{degraded}$ is the amount of the COD degraded in the reactor, $COD_{digestate}$ the amount of COD that was extracted with the digestate, $COD_{substrate}$ the amount of COD fed with the substrate and $COD_{reactor}$ the amount of COD that stays within the reactor. In order to evaluate the kinetics parameters for the actual rate - limiting step in the AD of HTC process water, Wirth et al. (2015b)) used a Chapman's model (Eq. 2.4.17) to fit the cumulative daily methane production during the phase of decay with a non-linear least squares routine (Pohl et al. 2012).

$$Y_{CH_4} = Y_{CH_4,max} \times \left(1 - e^{k_M \times t}\right)^c \quad (2.4.17)$$

where $Y_{CH_4,max}$ is the final maximum methane yield, t the time, k_M and c kinetics parameters. The model provided the methanogenesis kinetics constants. In their study, the authors only reported a kinetics constant, K_M, of 0.044 d^{-1} for the thermophilic AD of HTC process water (HTC process conditions 200 ℃ and 6 h). Treating HTC condensate from sewage sludge (HTC process conditions: 200 ℃ and 6 h), Wirth and Reza (2016) found a similar result for a thermophilic system (k_M = 0.049 d^{-1}), while the mesophilic system showed a much higher kinetics constant of 0.179 d^{-1}, indicating a slightly better process stability and performance of the mesophilic reactor compared to the thermophilic system. Following Eq. 2.4.17, Nyktari et al. (2017) calculated methanogenesis kinetics at different HTC conditions for the AD of HCT process water from sewage sludge. Results showed that as the HTC temperature and the HTC treatment time rise, the methanogenesis slowed down.

2.5 Energy Assessments

HTC was applied to sludge in order to evaluate an integrated AD-HTC system for bioenergy production (Reza et al. 2014). From the analysis of the specific literature, it can be deduced that lower HTC temperatures and treatment times promote biogas production from the HTC process water, while higher HTC temperatures and treatment times promote the carbonisation of sludge increasing its HHV and dewaterability (Danso-Boateng et al. 2015b; Escala et al. 2013; Nyktari et al. 2017). In order to integrate the HTC process with the sludge management, a compromise has to be found between biogas and hydrochar production, dewaterability

and energy consumptions. Several process configurations can be implemented in WWTPs as the HTC process can be applied as a treatment of primary sludge, activated sludge and digestate effluent. Among the HTC process conditions investigated by Danso-Boateng et al. (2015b), HTC at 180 ℃ for 60 min and 200 ℃ for 30 min proved to be the best operating conditions for integrating HTC process as a treatment of primary sludge and the AD of HTC process water. The following data were provided by the authors at those operating conditions: hydrochars yield of 66.3 – 70.2 %, a hydrochar HHV of 17.70 – 17.90 $MJ\ kg^{-1}$, energy yield of 73.0 – 76.9 % and carbon recovery of 57.8 – 60.7 %, together with methane yields from the HTC process waters of 50.3 – 61.3 %. According to Nyktari et al. (2017), HTC applied at 180 - 190 ℃ and residence times lower than 90 *min* could be a good compromise, in order to both improve the HHV of the hydrochar and its dewaterability and, at the same time, avoid the formation of not biodegradable or toxic compounds in HTC process water that can reduce biogas production during AD. Indeed, even though the soluble COD increases with the HTC temperature and the residence time, the biodegradable fraction decreases leading to a lower methane production (Aragón-Briceño et al. 2017). Danso-Boateng et al. (2015a) conducted an energy balance of a semi-continuous HTC process of faecal waste, conducted at 200 ℃ and at a reaction time of 30 min, based on recovering steam from the HTC process as well as energy from the solid fuel (hydrochar) and methane from digestion of HTC liquid product. Results showed a positive energy balance for human faecal wastes with a solid content higher than 15-25 %. Aragón-Briceño et al. (2017) found that higher levels of biogas production were obtained treating HTC process water from digestate sludge at lower HTC temperature (160 – 220 ℃), as compared to the results obtained at HTC temperature of 250 ℃. The same authors interestingly proved that HTC treatment enhanced the potential methane production in all products up to 58 % for both, the whole fractions (hydrochar + HTC process water) and HTC process water. In a process configuration including the AD of sewage sludge, followed by the HTC of digestate and the AD of HTC process water and hydrochar, the overall energy produced for unit of feedstock was 19.77, 18.88 and 17.96 $MJ\ kg^{-1}$, at HTC temperature of 160, 220 and 250 ℃, respectively (Aragón-Briceño et al. 2017).

2.6 Economic Assessments

In this review, many works with different combinations of HTC process and AD have been analysed, such as HTC of primary or secondary sludge separating the resulting hydrochar and valorising the HTC process water

by means of AD. Here, the authors want to propose a WWTP scheme for improving the economics of sludge disposal. In Figure 2.2, a comparison between a conventional sludge line and the new scheme is proposed. Considering the conventional sludge line (Figure 2.2 A), the final disposal of sludge in Northern Italy costs about 80-100 € per ton of sludge (Andreottola et al. 2006), typically at 20-25 % dry matter content, and similar numbers apply to Europe. In Figure 2.2 B a new sludge treatment line is proposed: after AD, digestate is dewatered at around 20 % dry matter content and then processed applying HTC at 190 ℃ for 1 h. The HTC slurry is then dewatered, thus the resulting hydrochar can reach values of dry matter content up to 70 % reducing its volume between three and four times (Escala et al. 2013; Yoshikawa and Prawisudha 2014). The thermal and electrical energy required by the whole HTC process (comprehensive of the following dewatering step) can be estimated, respectively, in 100 and 15 kWh per ton of sludge (TerraNova-Energy n.d.). Even when considering the hydrochar from sewage sludge as a waste to be disposed of, the HTC treatment allows for a significant reduction of the costs involved in sewage sludge management and disposal, with values as low as 42 € per ton of sewage sludge input according to an industrial player (TerraNova-Energy n.d.). Considering hydrochar for some applications, such as soil improver, adsorbent or as a resources for phosphorous recycling and reclamation (He et al. 2013; Weber et al. 2014; Zhao et al. 2014), the cost can be further reduced. Alternatively, if the local legislation allows the combustion of hydrochar, thermal energy could be also recovered in order to sustain the HTC process. It is of interest for the present review the economic energy analysis of the valorisation of HTC process water through AD, which can further increase the economics of the whole process: recycling back the process water to the anaerobic digester can lead to an increase of methane production, that can further sustain the thermal energy requirement of HTC process. Considering as the base line one ton of sludge at 20 % of dry matter content, processed by means of HTC, a solid yield of 85 %, a yield in organic liquids of 10 %, a gas yield of 5 % and a dry matter content of hydrochar up to 60 % after dewatering by centrifugation, 283 kg of hydrochar at 60 % of solid content and 707 kg of HTC process water are obtained (and 10 kg of gas, mainly CO_2). Assuming a COD concentration of the order of 35 $gCOD\ L^{-1}$ (Table 2.2,Wirth et al. (2015b)), the methane yield obtained in Wirth et al. (2015b) and reported in Table 2.5 equal to 0.144 $L\ CH_4\ gCOD^{-1}$, it's possible to compute a further methane production of 3.56 $m^3\ CH_4\ ton_{sludge}^{-1}$. Assuming conservatively a combustion thermal efficiency of 85 %, the produced methane can provide about 32 kWh per ton of treated sludge, covering about one third of the thermal requirement of HTC process, thus significantly reducing its operational

costs.

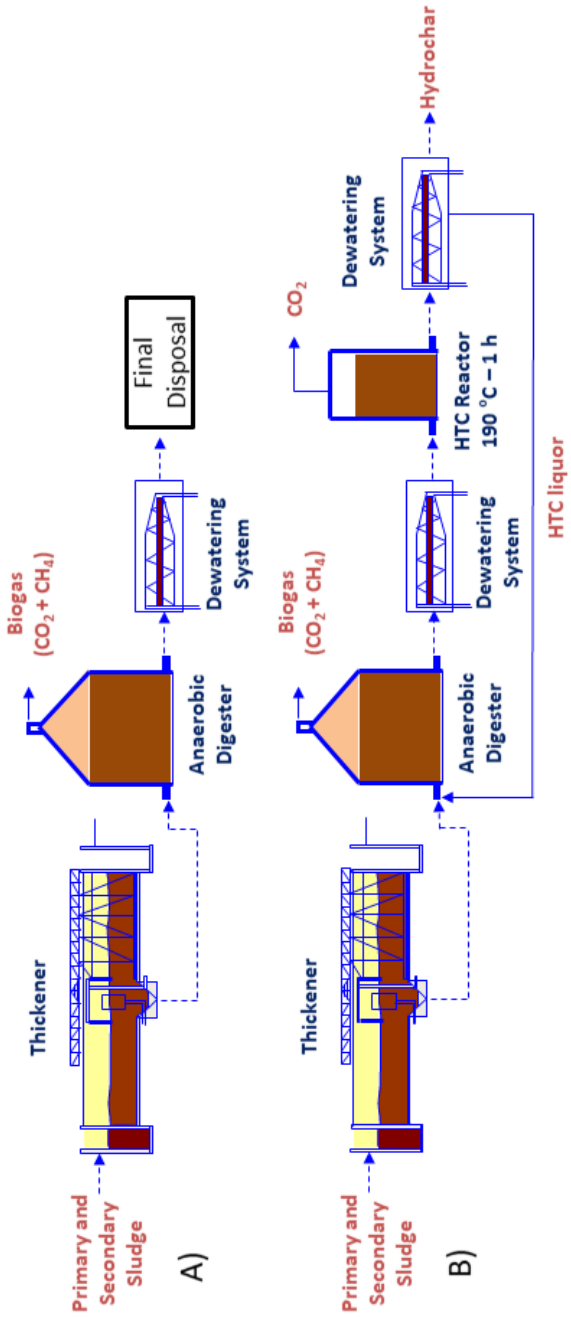

Figure 2.2: comparison between A) traditional sludge management and B) a new possible scenario coupling AD and HTC.

2.7 Conclusions

HTC of sewage sludge has a great potential to become a sustainable conversion process for the management of sludge and the production of a wide variety of valuable products. However, the liquor from HTC of sewage sludge represents a net output of the process and it has to be properly managed, treated and possibly valued, prior of its disposal. In this review, the valorisation of the resulting HTC process waters by means of AD has been analysed showing to be a promising option, both to sustain HTC thermal needs, through biogas combustion, and to reduce the environmental impacts of HTC process water disposal. Methane yield by AD of HTC process water from sewage sludge ranges between 0.022 – 0.277 $L\ CH_4\ gCOD^{-1}$. Microorganisms in the AD process could to some extent adapt to phenol or other toxic organic compounds, but further investigations on microbial community involved in AD of HTC liquor are required. HTC process temperature and residence time, initial feedstocks characteristics, nutrients concentration, inoculum acclimation and its buffer capacity result as the main parameters, which influence the performances of HTC process water valorisation through AD. Lack of nutrients in HTC process water, the presence of high concentrations of toxic compounds and high OLR can lead to AD process inhibition. In order both to produce hydrochar and to treat the HTC liquor through AD, the HTC temperature and treatment time should not be higher than 180 - 200 ℃ and 15 – 30 min, respectively, because higher temperatures and higher treatment time lead to the formation of not biodegradable and / or toxic compounds. Furthermore, a compromise between thermal efficiency and solid content of the treated sludge has to be found, because, even if sludge with a TS content higher than 15-25 % allows a positive energy balance of HTC-AD system, an overly concentrated sludge could lead to a large concentration of ammonia in the HTC liquor and cause the inhibition of the AD process. For a full-scale implementation of HTC process in a WWTP, further studies are needed, in order to investigate the effect of HTC process water on stable operations of AD, considering the fate of emerging contaminants and the long-term effects of recalcitrant and toxic compounds, which could accumulate in the whole system.

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Chapter 3

Hydrothermal Carbonisation of Biomass: Design of a Bench-Scale Reactor for Evaluating the Heat of Reaction

Chapter 1 and Chapter 2 are an introduction on HTC of sewage sludge and the valorisation of the solid and liquid streams, therefore the basic idea is to proceed first in the description of the reactor designed during my PhdD through this chapter and continue in the next chapters with the experimental work carried out having as basis the review chapters. In particular, this Chapter is a description of the reactor I designed in order to study Hydrothermal Carbonisation process and its heat of reaction and some preliminary results were presented in IconBM conference (Bologna, Italy, $17-20^{th}$ June 2018) and published in *Chemical Engineering Transactions* journal: Merzari F., Lucian M., Volpe M., Andreottola G., Fiori L., 2018, Hydrothermal carbonization of biomass: design of a bench-scale reactor for evaluating the heat of reaction, Chemical Engineering Transactions, 65, 43-48 DOI: 10.3303/CET1865008

Hydrothermal Carbonisation of Biomass: Design of a Bench-Scale Reactor for Evaluating the Heat of Reaction

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3.0 Abstract

HydroThermal Carbonization (HTC) is a thermochemical process capable of converting wet biomass into a carbon-enriched solid, commonly referred to as hydrochar. Hydrochar finds application as bio-fuel, soil improver and for the production of carbon-advanced materials. In recent years, interest in HTC technology has grown significantly, in terms of both scientific research and industrial development. The HTC process consists of several reactions occurring both in series and in parallel: hydrolysis, dehydration, decarboxylation, condensation, aromatization, and others. Some reactions are known to be exothermic, while others are endothermic. Knowing the enthalpy of the "whole" HTC reaction would be beneficial in terms of both process design and energy calculations, in particular to evaluate the process heat duty. Unfortunately, such kind of information is barely available in the literature: some data have been obtained at the "micro-scale" using differential scanning calorimetry (DSC), with the limits of using a few milligrams of (usually heterogeneous) biomass per trial, while punctual data at larger scale are actually missing. In order to fill this gap, we designed and constructed in-house a 2 L batch reactor equipped with four thermocouples - placed at different heights inside the reactor - and capable to withstand pressures up to 140 *bar* and temperatures up to 300 ℃. The reactor, controlled in temperature, is heated by four electrical resistances (1 kW each) and thermally insulated. An electric power meter allows monitoring and recording the electrical consumption during HTC trials. Thermal trials were performed with the bench-scale reactor fed with only water to provide a baseline for calculations. HTC trials were then performed using biomasses, namely organic fraction of municipal solid waste, sewage sludge and agave pulp. At the different HTC operating conditions investigated (residence time: 3 h; reactor filling degree: 67 %; temperatures: 180, 220, and 250 ℃; dry biomass to water ratio: 0.10, 0.07 and 0.15), our data testify that the "whole" HTC reaction is exothermic, and the heat released by the reac-

tion increases with temperature. The design of such a reactor and the data obtained so far encourage an in-depth analysis of the enthalpy of the HTC reaction for different biomasses and at various operating conditions.

3.1 Introduction

In recent years, HTC has attracted considerable attention as a promising process for treating several kinds of organic wastes. HTC occurs in liquid water at temperatures of 160-280 ℃ and residence times up to 8 h. It is particularly suitable for organic substrates with high moisture content and is interesting for several reasons: it makes wastes hydrophobic, enhancing their drying and storage properties, and increases their energy density, allowing their subsequent upgrading to fuels. Despite the substantial amount of research studies on HTC available in the literature, only few of them addressed the evaluation of the heat released (or consumed) by the chemical reactions occurring during HTC or, similarly, the heat of the "whole" HTC reaction. Although the energy efficiency is largely influenced by the thermal requirements needed to pre-heat the biomass and by the heat recovery system of the plant (Lucian and Fiori 2017), also the heat of reaction could have a significant impact. Some researchers calculated the heat of reaction from the heats of formation of reactants and products, but reported results with a defined uncertainty (Sunner and Wadsö 1961; Yan et al. 2010). Funke and Ziegler (2011) measured the heat of reaction performing HTC tests in a DSC apparatus using three substrates (glucose, cellulose and wood) at a temperature of 240 ℃ for 4-6 h. Their results show that HTC was exothermic in all the analysed cases, and the measured heat of reaction was equal to -1.06, -1.07 and -0.76 $MJ\ kg^{-1}$ for glucose, cellulose and wood, respectively. Notably, such values were characterized by a high standard deviation, in the range 14 – 32 %. The limit of the approach by Funke and Ziegler (2011) is the apparatus used which required very small amount of sample (few milligram) for the tests. The aim of this paper is to evaluate the heat of the HTC reaction using a bench-scale reactor, properly designed and constructed in-house for the purpose. The heat of reaction was determined performing HTC trials on three kinds of biomasses: agave pulp, sewage sludge and organic fraction of municipal solid waste.

3.2 Materials and methods

3.2.1 Experimental apparatus

A HTC experimental system was designed at the Department of Civil, Environmental and Mechanical Engineering of the University of Trento (Italy) and constructed in-house at the mechanical workshop of the University of Trento according to the European standard UNI EN 13445-3:2014 concerning unfired pressure vessels. The system is composed of two main parts, namely the HTC reactor and the gas measuring system: the left part of Figure 3.4 shows the piping and instrumentation diagram (P&ID) of the whole system. The HTC reactor consists of a stainless steel AISI 316 batch vessel of 2 L internal volume. The right part of Figure 3.4 shows 2D and 3D technical drawings of the HTC reactor, while Figure 3.1 shows a picture of the apparatus. The reactor was designed to withstand temperatures up to 300 ℃ and pressures up to 140 bar. A gasket (which can be either copper or Teflon) allows sealing between the reactor body and the top flange. The top flange of the reactor is connected to two pipes (2 mm internal diameter), which allow air purging through the needle valves V1 and V2 by flowing nitrogen gas. Since the HTC process is usually carried out between 180 ℃ and 250 ℃, a cold trap was added to the left pipe to protect the pressure transmitter (PT) and the two pressure gauges (PI) from high temperature and avoid any clogging. A rupture disk is positioned in the same pipe, upstream one PI, in order to protect the HTC reactor from pressures greater than the design one and for safety reasons. The temperature inside the reactor is measured by four thermocouples (T1, T2, T3, T4) that pass through the reactor top flange and are positioned at different heights within the reactor. The temperature transmitters (TT) and the pressure transmitter (PT) send data to a software realized in-house in LabView software environment as showed in Figure 3.2. The software allows the control of the reactor temperature (TIC) and the monitoring of the four temperatures and the pressure (TIR and PIR). The reactor is heated by four electrical resistances (1 kW each) inserted into two aluminium shells. Such shells allow an efficient heat transfer on the entire external cylindrical walls of the reactor. The aluminium shells have externally a layer of insulating material to limit thermal dissipation. The shells are equipped with mechanical hinges: during the test (heating phase and constant temperature phase) the shells are tightened on the reactor; once the test is over, the shells are opened to allow the reactor to cool down. Figure 3.1 shows the reactor with the shells in open position. An electric power meter allows monitoring and recording the electrical consumption during HTC trials (Figure 3.2): through this measure, data concerning the heat of

Figure 3.1: HTC reactor.

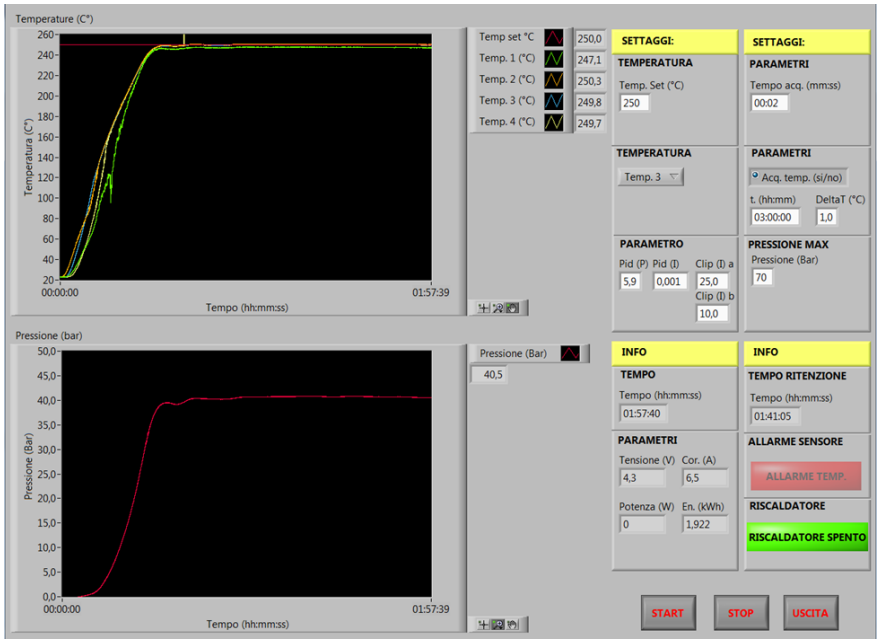

Figure 3.2: Labview interface that allows the measurement of temperature, pressure, residence time and electric consumptions.

reaction could be inferred. When the HTC run is finished, the reactor is cooled down by placing a massive metal disk (at -24 °C) on its bottom and by flowing compressed air on its external walls. When the reactor reaches room temperature, the produced gas is flowed to the gas volume

measuring system by opening valve V2. The gas volume measuring system consists of a PVC graduated cylinder with the lower part submerged into water (see P&ID in Figure 3.4). Before the measurement, a vacuum pump raises the water meniscus up to the zero of the graduated scale. When the produced gas enters into the graduated cylinder, it displaces a certain water volume allowing calculating its own volume.

3.2.2 Experimental campaign and procedure

The experimental trials presented in this work were aimed at obtaining information on the heat of the HTC reaction. Experimental runs were conducted at three temperatures, namely 180, 220 and 250 ℃. Residence time and reactor filling degree were maintained constant at 3 h and 67 %, respectively. T different biomasses were tested, namely agave pulp (AP), sewage sludge (SS) and organic fraction of municipal solid waste (OFMSW). The dry biomass to water ratio (b/w) was let equal to 0.10 for AP, 0.07 for SS and 0.15 for OFMSW. Tests at each experimental condition were performed at least in duplicate. Raw biomass and deionized water were accurately inserted into the HTC reactor in order to achieve the chosen b/w and reactor filling degree (sewage sludge was used as received). The reactor was then sealed and nitrogen gas was fluxed for about 3 min through the system to purge it from air. After purging, V1 and V2 valves were closed, and the heating phase started: around 30-35 min were necessary to reach the desired temperature set point. Residence time was started to be counted when the reactor temperature (read from thermocouple T3) reached the set point value. When the 3 h residence time was elapsed, the control system automatically stopped the power supply. The reactor shells were then manually opened, and the reactor cooled down. The quenching phase lasted about 25-30 min, depending on the HTC process temperature. The volume of the gas produced was then measured. The reactor was opened (i.e. the reactor body was disconnected from the reactor top flange) and its content was filtered through a dry cellulose filter, and both hydrochar and HTC liquor were collected. Hydrochar, the relevant cellulose filter, and the reactor body were placed inside an oven at 105 ℃ for at least 8 h. After drying and weighing, the hydrochar yield (solid yield, SY) was computed as the ratio between the mass of hydrochar produced and the initial mass of the feedstock ($g_{hydrochar}\ g_{feedstock}^{-1}$, both on dry basis). The hydrochars were characterized in terms of ultimate and proximate analyses, and higher heating value (HHV). Gas yield (GY, $g_{gas}\ g_{feedstock}^{-1}$, both on dry basis) was computed by means of the ideal gas law, assuming atmospheric pressure, ambient temperature and only CO_2 as the gaseous product (Basso et al. 2016). The liquid yield (LY, $g_{liquid}\ g_{feedstock}^{-1}$), due species dissolved

in the HTC liquor owing to feedstock decomposition, was calculated by difference ($LY = 1 - SY - GY$). In order to assess the heat of reaction of the whole HTC process, some experimental runs with deionized water were performed at the same experimental conditions used for the biomasses: 180, 220 and 250 °C, 3 h of residence time and 67 % of reactor filling degree. The electrical power consumptions of these tests were used as the baseline to compute the actual heats of the HTC reaction at the different operating conditions investigated.

3.2.3 Calculation

The electric power meter allows monitoring and recording the electrical consumption during HTC trials. The heat of reaction was computed separating the constant temperature phase (zone 2 of Figure 3.3) from the transient phase occurring during the initial heating up of the apparatus (zone 1 of 3.3). Concerning the constant temperature phase, the net en-

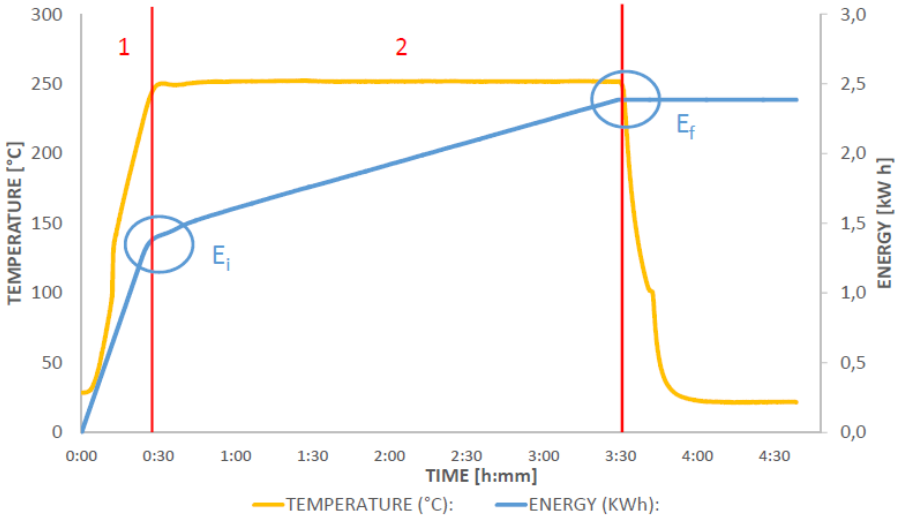

Figure 3.3: typical HTC profile Temperature and its Electrical Consumption.

ergy consumption (E_{net}) was calculated as the final energy consumption of the HTC process after 3 h of residence time (E_f as reported in Figure 3.3) minus the energy consumption of the transient phase (E_i as showed in Figure 3.3) as reported in Eq.3.2.1.

$$E_{net} = E_f - E_i \tag{3.2.1}$$

After the thermal trials, E_{net} for biomasses and water were available (E_{net} for water is due to thermal losses), so Eq. 3.2.2 allows computing

the energy duty (energy produced or consumed) of the HTC process occurring at constant temperature.

$$E_{duty(T=constant)} = E_{net,biomass} - E_{net,water} \tag{3.2.2}$$

Dividing the energy duty by the initial amount of dry feedstock ($M_{dry\ feedstock}$), it is possible to compute the heat of reaction concerning the constant temperature phase, Eq.3.2.3.

$$Heat\ of\ reaction_{T=constant} = \frac{E_{duty(T=constant)}}{M_{dry\ feedstock}} \tag{3.2.3}$$

Concerning the heating up phase, Eq. 3.2.4 provides the theoretical sensible heat required to heat the biomass/water mixture or, eventually, the water for the tests performed with only deionized water.

$$\begin{aligned} &Theoretical\ sensible\ heat = E_{theor} = \\ &= c_p \cdot m \cdot (T_{HTC} - T_{ambient}) \end{aligned} \tag{3.2.4}$$

In Eq. 3.2.4, c_p is the specific heat, m is the mass charged into the reactor, T_{HTC} is the HTC set point temperature and $T_{ambient}$ is the temperature of the system before power is applied to heat it. At first, tests with only deionized water were performed. By comparing, for such tests, the energy consumption of the transient phase (E_i) with the value from Eq. 3.2.4, it was possible to infer the energy losses Q^* occurring during the heating up phase as showed in Eq. 3.2.5.

$$Energy\ losses = Q^* = E_{i,water} - E_{theor,water} \tag{3.2.5}$$

Reasonably, such values of energy losses were considered to apply also for the tests where biomass/water mixtures were used. For such HTC tests, E_i was experimentally measured, Eq. 3.2.4 was used to calculate the sensible heat, thermal losses known, it was possible to calculate the energy duty $E_{duty-transient}$ concerning the heating-up phase as showed in Eq. 3.2.6.

$$E_{duty-transient} = E_{i,biomass} - E_{theor,biomass} - Q^* \tag{3.2.6}$$

Notably, when applying Eq.3.2.4 to biomass/water mixtures, the amounts of water and biomass (actually, dry biomass) were calculated considering the experimental values of dry biomass to water ratio; whatever the biomass used (OFMSW or AP), its c_p was assumed equal to 1.26 $kJ\ kg^{-1}\ K^{-1}$, which is a first approximation reference value for dry organic matter. It was thus possible to compute the heat of reaction concerning the transient temperature phase, Eq. 3.2.7.

$$Heat\ of\ reaction_{transient} = \frac{E_{duty-transient}}{M_{dry\ feedstock}} \tag{3.2.7}$$

The total heat of reaction is the sum of the two contributes as reported in Eq. 3.2.8.

$$\begin{aligned} &Heat\ of\ reaction\ = \\ &= Heat\ of\ reaction_{T=constant}\ +\ Heat\ of\ reaction_{transient} \end{aligned} \tag{3.2.8}$$

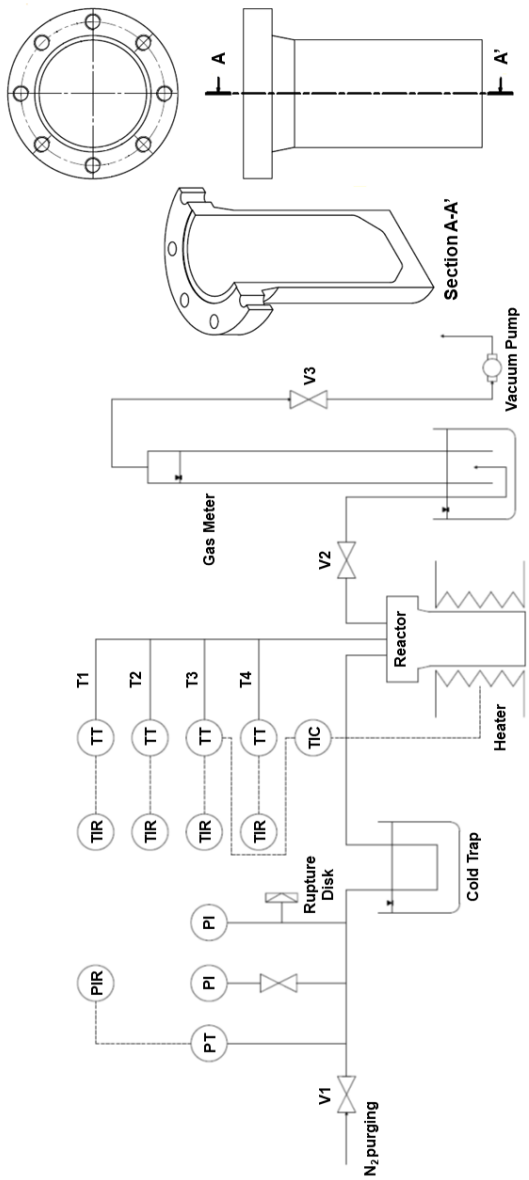

Figure 3.4: P&ID of the experimental apparatus and technical drawings of the HTC reactor.

3.3 Results and discussion

Table 3.1 shows the yields of hydrochar, liquid and gas for each operative conditions for AP, SS and OFMSW. As expected from literature, the hydrochar yield decreases with the increase of temperature, while gas yield has an opposite trend (Fiori et al. 2014; Basso et al. 2015; Basso et al. 2016; Volpe and Fiori 2017; Volpe et al. 2018). Concerning agave pulp, solid yield decreases from 54.2 % at 180 °C down to 34.8 % at 250 °C. Liquid and gas yield were not computed for SS and OFSMW, and the hydrochar yields for SS and OFMSW were similar to the hydrochar yield obtained for AP at the same temperature. For AP, gas yield increases from 5.5 % at 180 °C up to 20.4 % at 250 °C.

Table 3.1: Hydrochar, liquid and gas yields for the tests performed.

Sample	SY ($\%_{d.b.}$)	LY ($\%_{d.b.}$)	GY ($\%_{d.b.}$)
AP 180 °C	54.2	37.3	5.5
AP 220 °C	50.9	32.3	16.8
AP 250 °C	34.8	44.8	20.4
OFMSW 220 °C	54.8	-	-
SS 220 °C	57.4	-	-

Table 3.2 shows the higher heating values (HHVs) and the ultimate and proximate analyses of raw dry biomasses and hydrochars, and the heats of the HTC reaction. It is possible to observe that the carbon content, the fixed carbon (FC), the HHV, and the heat of reaction increase with HTC temperature, and conversely the oxygen content, the volatile matter (VM) and the ash content decrease. Hydrogen and nitrogen seem quite independent on HTC temperature. Carbon content, for the agave pulp, increased from 48.27 % for the raw feedstock, up to 53.75 % for the hydrochar obtained at 250 °C, while for the OFMSW increased from 51.98 % for the raw substrate to 66.66 % for the hydrochar obtained at 220 °C. Concerning SS, carbon content increased from 40.38 % for the raw sludge to 46.09 % for the hydrochar obtained at 220 °C. HHV for the agave pulp increased from 16.58 $MJ\ kg_{d.b.}^{-1}$ for the raw feedstock, up to 24.56 $MJ\ kg_{d.b.}^{-1}$ for the hydrochar obtained at 250 °C. For the OFMSW, HHV increased from 22.00 $MJ\ kg_{d.b.}^{-1}$ for the raw substrate to 29.90 $MJ\ kg_{d.b.}^{-1}$ for the hydrochar obtained at 220 °C. For SS, HHV increased from 15.78 $MJ\ kg_{d.b.}^{-1}$ to 18.63 $MJ\ kg_{d.b.}^{-1}$ for the hydrochar obtained at 220 °C. In Figure 3.5, the energy consumption of the HTC trials performed at 220 °C, 3 h and 67 % of filling degree is reported. It is possible to observe that the water has the highest energy consumption (highest curve in Figure 3.5), while OFMSW has the lowest energy consumption (lowest curve in

Figure 3.5): the HTC reaction makes the energy consumption to decrease, i.e. the "whole" HTC reaction is exothermic. Quantitative data of the heat of reaction are reported in Table 3.2. Heat of reactions are negative, i.e. the HTC reaction is exothermic in all the cases investigated: in Figure 3.6 is reported the evolution in time of the heat of reaction for the HTC trials performed at 220 ℃ that testified the exothermal behaviour of HTC process.

For the agave pulp, the heat of reaction increases from -1.0 $MJ\ kg_{d.b.}^{-1}$ computed from the experimental run at 180 ℃, up to -3.9 $MJ\ kg_{d.b.}^{-1}$ computed from the run at 250 ℃. The heat of reaction is maximal for the HTC of OFMSW: -7.3 $MJ\ kg_{d.b.}^{-1}$, while for SS heat of reaction is -4.0 $MJ\ kg_{d.b.}^{-1}$. The exothermal character of the HTC reaction here found is in agreement with what reported by Funke and Ziegler (2010). Interestingly, the data here presented testify that the heat released by the HTC reaction increases with temperature. It is not possible to make straightforward comparisons with data from literature, given their scarcity. Given this premise, it is worth reporting the results by (Funke and Ziegler 2011) who obtained heat reaction data using differential scanning calorimetry for cellulose, glucose and wood. The authors performed tests at 240 ℃and 4-6 h obtaining values between -0.76 and -1.07 $MJ\ kg_{d.b.}^{-1}$, using a few milligrams of feedstock per trial. Our data confirm the exothermal character of the HTC reaction previously detected by Funke and Ziegler (2011).

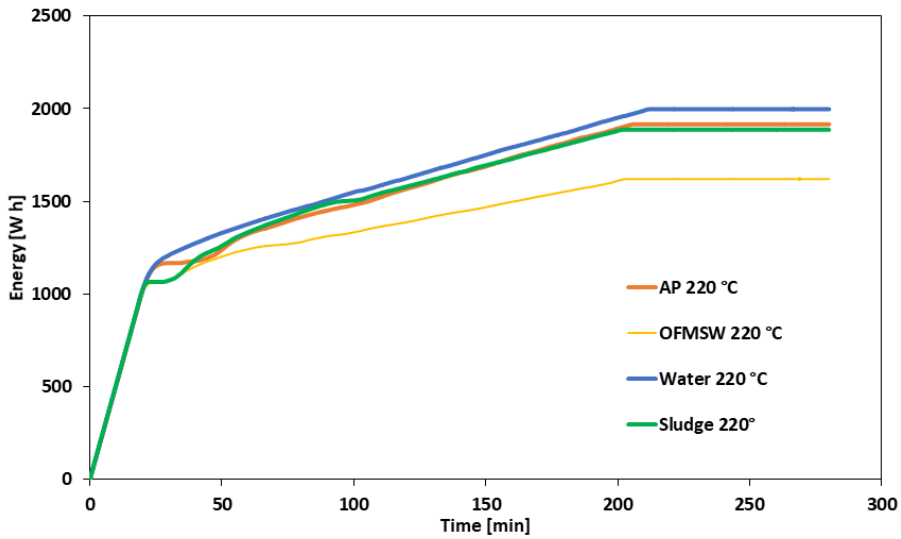

Figure 3.5: energy consumption measured at 220 ℃ and 3 h with agave pulp, OFMSW, sludge and water.

Table 3.2: Heats of reaction, ultimate and proximate analyses, higher heating values of raw dry biomasses and hydrochars.

Sample	**C** ($\%_{d.b.}$)	**H** ($\%_{d.b.}$)	**N** ($\%_{d.b.}$)	**O** ($\%_{d.b.}$)	**Ash** ($\%_{d.b.}$)	**VM** ($\%_{d.b.}$)	**FC** ($\%_{d.b.}$)	**HHV** ($MJ\ kg^{-1}_{d.b.}$)	**Heat of reaction** ($MJ\ kg^{-1}_{d.b.}$)
Raw AP	48.27	6.12	1.47	42.05	2.08	77.9	20.02	16.58	-
AP 180 °C	48.73	6.16	1.63	40.4	3.28	73.92	22.8	19.51	-1
AP 220 °C	50.38	6.26	1.44	39.21	2.76	71.07	26.17	21.51	-3.1
AP 250 °C	53.75	6.21	1.49	36.87	1.52	64.07	34.41	24.56	-3.9
Raw OFMSW	51.98	6.71	3.58	32.33	5.4	80.7	13.9	22	-
OFMSW 220 °C	66.66	7.05	3.65	16.8	5.84	69.5	24.7	29.9	-7.3
Raw SS	40.38	5.00	2.26	27.46	24.9	65.37	9.73	15.78	-
SS 220 °C	46.09	4.90	2.51	26.13	20.37	61.00	18.63	18.93	-4.0

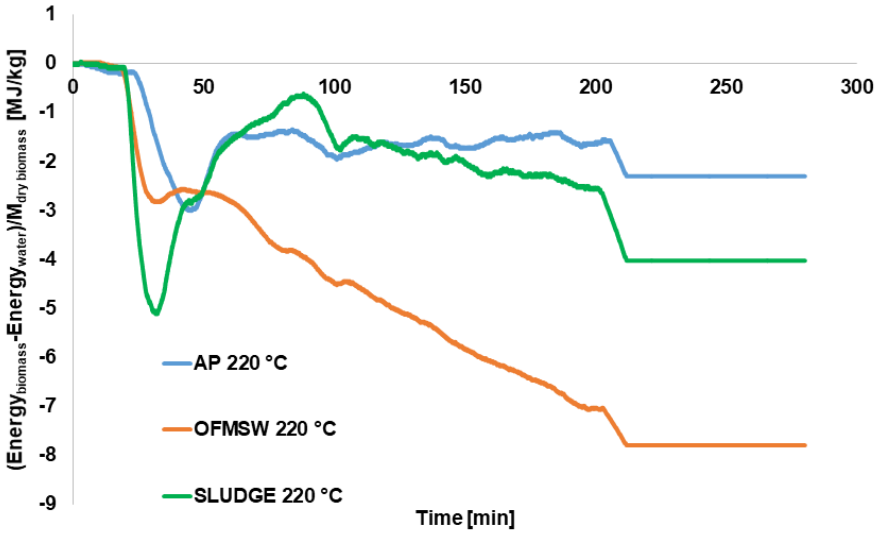

Figure 3.6: Heat of reaction in function of time computed at 220 ℃ and 3 h with agave pulp, OFMSW and sludge.

3.4 Conclusions

HTC experimental trials were performed in a bench-scale reactor using two biomasses, namely organic fraction of municipal solid waste, sewage sludge and agave pulp at different HTC operating conditions (residence time: 3 h; reactor filling degree: 67 %; temperatures: 180, 220, and 250 ℃; dry biomass to water ratio: 0.10, 0.07 and 0.15). The data reported in this work testify that HTC is an exothermic process, and the heat released by the reaction increases with temperature: from -1.0 MJ $MJ\ kg_{d.b.}^{-1}$ at 180 ℃, to -3.9 $MJ\ kg_{d.b.}^{-1}$ at 250 ℃ for agave pulp, while for the OFMSW and SS the heats of reaction at 220 ℃ were as high as -7.3 $MJ\ kg_{d.b.}^{-1}$ and -4.0 $MJ\ kg_{d.b.}^{-1}$ respectively. The data obtained encourage an in-depth analysis of the heat of reaction of the HTC process for other biomasses and operative conditions, such as residence time, temperature, and biomass load. Having an in-depth knowledge of the heat of reaction of the process allows more accuracy in the process modelling and therefore to carry out a more adequate design, better estimating thermal consumptions.

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Chapter 4

Hydrothermal Carbonisation as a Thermal Treatment Strategy for Sewage Sludge Management

This Chapter reports the main research activity I performed concerning hydrothermal carbonisation of sewage sludge, providing the characterisation of solid and liquid phases and the assessment of their potential valorisation. The Chapter follows the design of the HTC reactor,but the construction took almost 2 years, so the HTC runs were carried out through a smaller reactor. Part of results were presented in "Biochar: production, Characterization and Application" conference (Alba, Italy, $20-25^{th}$ August 2017)

Hydrothermal Carbonisation as a Thermal Treatment Strategy for Sewage Sludge Management

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4.0 Abstract

Conventional Activated Sludge (CAS) systems have been widely implemented to treat wastewater. CAS systems produce huge amounts of waste sludge and its subsequent treatment represents up to 65 % of the operational costs of Waste Water Treatment Plants. The final disposal of sludge is usually performed by landfilling or incineration, involving severe environmental issues. In order to reduce sludge amount, many studies have been conducted, developing new technologies. One of these technologies is Hydro Thermal Carbonisation (HTC), where sludge is heated up to 180-250 ℃ at water vapour pressure producing a solid product enriched in carbon for different possible exploitations. The aim of this work is to apply HTC to different kinds of sludge such as thickened sludge, digested sludge and dewatered sludge and compare the behaviour of the solid and liquid phases produced by the process. For the purpose, experimental tests were performed at different operating conditions in a lab batch reactor capable to withstand high pressure (140 *bar*) and temperature (300 ℃). In order to compare the HTC products of the different kinds of sludge, the hydrochars from HTC at different operative conditions were characterized in terms of ultimate, proximate and ICP-OES analyses, while the liquid phase was characterized in terms of COD, pH, Nitrogen compounds and phosphorous.

4.1 Introduction

In 1991 European Union (EU) Directive 91/271/EEC set new benchmarks for the collection, treatment and monitoring of wastewater in urban areas (Steichen 1991). By 2000, the EU produced over 10 million dry tons of sewage sludge (the U.S. alone produced 7 million dry tons that year), increasing burdens on municipal wastewater treatment systems (EUROSTAT 2017). Yet, a 2016 report by the European Commission suggested that the 1991 directive was successful in terms of current improvements seen in EU water quality despite such growth, but notes that we must develop "innovative solutions to increase resource efficiency, such as solutions for energy recovery, nutrient recovery and processing to marketable products and water re-use (Commission 2016)". Beyond the EU, global urbanization and growth of the middle class, combined with stricter environmental regulations have forced municipalities to re-examine their sludge management practices – transitioning away from traditional disposal via incineration, landfilling or discharge to oceans/waterways – to favour beneficial reuse (Campbell et al. 2018; Yanagida et al. 2010). Sludge is a complex, heterogeneous mixture com-

prised of organic compounds such as proteins, peptides, liquids, polysaccharides, phenols, aliphatics, aromatics and furans, as well as inorganics such as nutrients (phosphorous, potassium, nitrogen), silica and heavy metals (Commission n.d.) and pathogens and other microbiological pollutants (Rulkens 2008). In a typical wastewater treatment process, primary sludge is characterized as the sludge following mechanical processing (screening, grit removal, sedimentation) containing between 93 to upwards of 99.5 % water, with a high content of suspended and dissolved organics. Secondary sludge (also known as Waste Activated Sludge, WAS) follows from biological treatment, and contains a high amount of microbial cells with a total solids concentration ranging between 0.8 and 1.2 % depending on the type of process used (Tyagi and Lo 2013). Anaerobic digestion is the most widely used sludge management technique; it converts the organic solids to biogas (predominantly CH_4 and CO_2) via hydrolysis, acidogenesis, acetogenesis, acidogenesis and methanogenesis (Cao and Pawłowski 2012). Despite its popularity, a considerable amount of solid remains after anaerobic digestion; as little as 20-30 % of organic matter is mineralized (Rulkens 2008). While these solids were once thought to be environmentally benign, their land application may well be a potentially large source of greenhouse gas emissions, point pollutant sources for mercury, lead, cadmium and copper on arable land, contribute to environmental acidification (Johansson et al. 2008) and pose a toxicological risk in terms of pathogens present (Rulkens 2008). The microbiological processes occurring on land-applied sludge (mainly anaerobic decomposition, nitrification and denitrification) lead to considerable emissions of methane and nitrous oxide, as well as ammonia and nitrate. While land application of sludge offsets the use of industrial nitrogen-containing fertilizers, and representing a considerable net reduction of N_2O, NH_3 and NO_3^- emissions, CH_4 emissions are still estimated to be higher at 6.3 $kg\ ton^{-1}$ of applied sludge (Johansson et al. 2008). As such, direct land application of secondary sludge may not be the optimal nutrient recovery pathway, and may well represent a waste of a renewable energy source. Hydrothermal carbonization (HTC) is a process to densify the carbon in a given biomass, occurring in water at elevated temperatures above the saturation pressure, where water's dielectric constant decreases so drastically that it acts as a reactant and organic solvent. It proceeds via a series of mechanisms, including hydrolysis, dehydration, dehydrogenation decarboxylation, demethanation, and oxidation. HTC is performed in 80 to 95 vol % water (Lucian et al. 2018; Lucian and Fiori 2017), making it an ideal processing pathway for wet biomasses such as sewage sludge. Not only does it lead to reduced volume and energy densification of the solid, in terms of sewage sludge HTC has been shown to considerably improve dewaterability (Zhao et al. 2014; Yoshikawa and Prawisudha 2014), sig-

nificantly increasing the ability to use hydrochars produced as solid fuels in combustion processes for energy generation, as well as to stabilize and disinfect sludge (Catallo and Comeaux 2008; Khalil et al. 2005). While primary and secondary sludge can be combusted without further treatment, HTC of sludge enhances $NO + NH_3$ reactions during solid combustion, significantly reducing NO_x emissions across combustion modes (Zhao et al. 2015). While multiple studies probe the impact of processing conditions on the solid and energy yields of hydrochars produced from the hydrothermal carbonization of sludge from one with drawl point in the WWT process (Danso-Boateng et al. 2015; Brookman et al. 2018; Breulmann et al. 2017; Liu et al. 2018; Zhao et al. 2014), the impact of upstream WWT processes on hydrochars is often not part of the experimental design. Thus, a primary goal of the present work was to determine the most viable point in the wastewater treatment (WWT) process to employ HTC for sludge treatment from an energy production and potential nutrient recovery standpoint. There are two sets of variables of interest in the present work: (1) feedstock with drawl point from the WWT process; (2) hydrothermal reaction conditions on the composition and oxidation properties of resulting hydrochars. While some research has been done to quantify the environmental and economic benefits of using HTC to treat sewage sludge, understanding the impact of both feedstock and processing conditions on resulting hydrochars is critical better enable optimization of this waste-to-energy conversion pathway (Vardon et al. 2011).

4.2 Material and Methods

Three different samples were collected at three process points from the municipal wastewater treatment plant (WWTP) of Trento, Italy, which uses a Conventional Activated Sludge (CAS) and Membrane BioReactor (MBR) system. The primary sludge extracted from the primary settler is sent to a static thickener and mixed with secondary sludge coming from the MBR system (Pipe 1 of Figure 4.1). The secondary sludge coming from the CAS system is sent to a dynamic thickener (Pipe 2). The outlets of Pipes 1 and 2 are combined as the Thickened Sludge feedstock (Pipe 3); this is the first sample taken for the present work. Anaerobic digestion of this thickened sludge lasts 21 days at 33 °C, after which the Digested Sludge (Pipe 4) is sent to a dewatering system (belt-press or centrifuge). The effluent from Pipe 4 is the second sample taken for this work. To the digested sludge from Pipe 4 polyelectrolyte is added; this stream is sent to the dewatering system. The dewatered digestate is centrifuged where it reaches about 25 % solids content to enable solid handling. This

dewatered sludge was sampled after the centrifuge (Pipe 5) as the third sample. Each of the three samples taken were characterized and stored in a fridge at 4 ℃ until use.

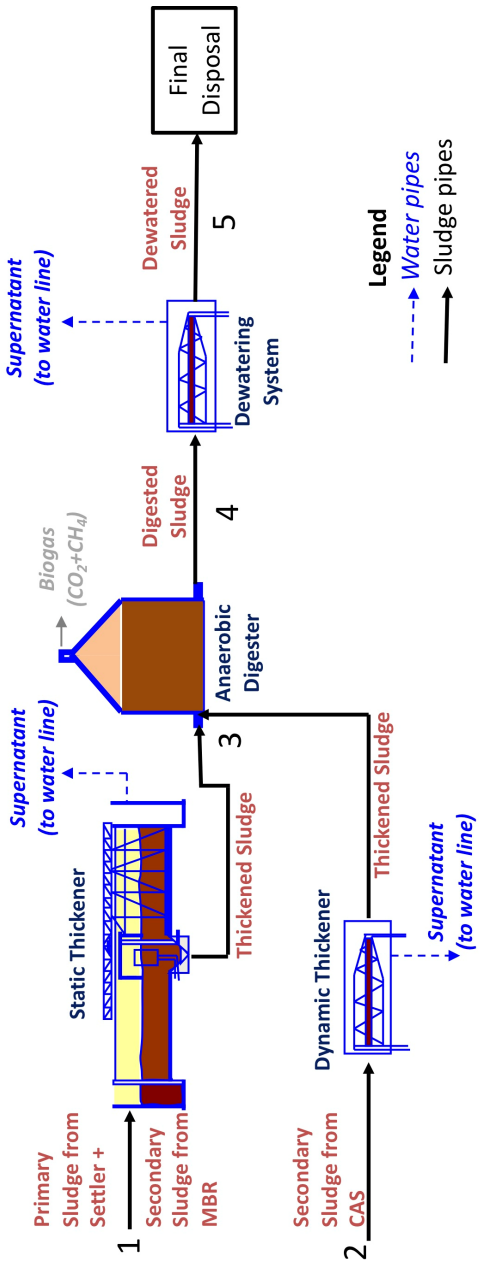

Figure 4.1: schematic of wastewater treatment plant in Trento, Italy identifying three sludge samples (Thickened – Pipe 3; Digested – Pipe 4; Dewatered – Pipe 5) used in the present work.

4.2.1 Feedstock Characterization

The three feedstocks used were characterized in accordance with accepted environmental practices. All measurements were conducted in triplicate and the average and standard deviation of each is reported. The total solids content of each sludge was measured by drying three samples of each substrate in an oven at 105 ℃ for at least 8 h until constant weight was reached. Following EPA Method 1684, the fixed and volatile solids content was determined by heating the dry solids in a muffle furnace at 550 ℃ for at least 8 hours. The pH was measured using a Profi-Line pH 3310 portable pH-meter. The total COD was measured using a closed reflux titration method using potassium dichromate digestion solution, sulfuric acid reagent, ferroin indicator solution and a standard ferrous ammonium sulphate titrant according to standard procedures. The same method was used for soluble COD following filtration of the sample through a 0.45 μm filter (APHA 2012). Organic nitrogen in the trinegative state was measured via the semi-micro Kjeldahl method (APHA 2012). Ammonium nitrogen were measured by first buffering the sample at pH 9.5 with a borate buffer (to decrease hydrolysis) then distilled in a solution of boric acid and the concentration determined via acid titration with H_2SO_4 (APHA 2012). To measure the total phosphorous, samples were first digested in H_2SO_4, forming molybdophosphoric acid, which is then reduced by stannous chloride to molybdenum blue. Concentration was measured photometrically at 690 nm and compared against a calibration curve (APHA 2012). Ultimate analysis to determine elemental composition of C, H, N, S and O (by difference) was conducted on a LECO 628 analyzer equipped with Sulphur module for CHN (ASTM D-5373 standard method) and S (ASTM D-1552 standard method) determination. Proximate analyses were done on a LECO Thermogravimetric Analyser TGA 701. Samples were heated at 20 min^{-} to 105 ℃ in air and held until constant weight ($< \pm 0.05$ %) to provide a dry baseline. They were subsequently heated at 16 min^{-1} from 105 ℃ to 900 ℃ in nitrogen with a hold time of 7 min, where the mass loss was attributed to volatile matter, VM. Finally, the sample was held at 800 ℃ in air to oxidize the fixed carbon, FC. Mass remaining after this is considered to be ash (inorganic matter) content. The higher heating value was measured using an IKA 200C isoperibolic calorimeter according to the CEN/TS 14918 standard. Inductively coupled plasma-optical emission spectroscopy (Spectro Arcos, Spectro, Germany) was used to determine the inorganic concentration of the sludge samples. Briefly, samples were oven dried at 105 ℃ until constant weight, and then acid digested in concentrated nitric acid using a single reaction chamber microwave digestion system (UltraWAVE, Milestone Inc., Sheldon CT USA) using Teflon-lined vials to pre-

vent interference. Elements were quantified using certified multi-element standards (CPI International).

4.2.2 Hydrothermal Carbonization and Product Analysis

Hydrothermal carbonization typically occurs between 180 and 250 ℃ under autogeneous pressure (up to 50 *bar*), but below the critical point (Lucian and Fiori 2017). The present work utilized a standard 50 mL stainless steel batch reactor rated to withstand 300 ℃ and 140 *bar*, with constant temperature and pressure monitoring, as described previously (Fiori et al. 2014; Basso et al. 2015; Basso et al. 2016). The thickened and digested sludges were used as-received, loading the reactor with 35.0 ± 0.1 mL biomass, which maintained a biomass (dry biomass) to water ratio of about 0.03:1. The dewatered sludge had a solid content of 25 % and needed to be dilute to insure that the biomass was fully submerged. The reactor was filled with 20.00 ± 0.01 g of dewatered sludge and 15.00 ± 0.01 g of deionized water to cover the sludge, resulting in a biomass to water ratio of 0.17:1. Prior to each run, the reactor was sealed and purged with nitrogen gas. It was heated to the desired reaction temperature (190, 220, or 250 ℃) and held at the set point for the desired reaction time (30 or 60 minutes). At least three experimental runs for each of the six temperature/time combinations were performed for each of the three sludge samples. After the reaction time, the reactor was cooled by placing stainless steel disks on the bottom and blocking compressed air into the outer walls. The reactor was cooled to ambient in less than 15 minutes, at which point the produced was measured by flowing it into a graduate cylinder. It is assumed that the gas is comprised entirely of CO_2 given literature showing that the CO_2 content is always greater than 90 vol % (Basso et al. 2015; Basso et al. 2016). The gas yield (Eq. 4.2.1) was estimated according to the ideal gas law under the assumption of standard temperature and pressure as:

$$Y_{gas} = \frac{Mass_{CO_2}}{Mass_{dry\ sludge}} \tag{4.2.1}$$

The liquid and solid products were filtered through a pre-dried and weighed piece of cellulose filter paper. The filter paper was then put in the oven overnight at 105 ℃ and weighed to calculate the solids produced. The solid yield of the hydrochar, $Y_{hydrochar}$, was calculated as described in Eq. 4.2.2:

$$Y_{hydrochar} = \frac{Mass_{dry\ hydrochar}}{} \tag{4.2.2}$$

The solid hydrochar was characterized according to the same methods described in Section 4.2.1 for higher heating value (HHV), proximate and

ultimate analyses. The hydrochar relative solid reactivity was measured used a Mettler-Toledo Thermograviemtric Analyzer-Differential Scanning Calorimeter (TGA-DSC-1) in an oxidative atmosphere. The TGA - DSC was calibrated with NIST-traceable gold, indium and aluminum and measured mass to the mass to the $\pm$ 0.1 μg and temperature to the $\pm$ 0.1 ℃. Approximately 10 mg of sample was loaded into a 70 μL alumina crucible. Samples were heated at 20 ℃ min^{-1} up to 110 ℃ in air flowing at 50 $mL\ min^{-1}$ and held for 30 minutes to drive off any residual moisture. They were subsequently heated at 20 textcelsius min^{-1} up to 950 ℃and held for 30 minutes to oxidize all material. The mass fraction of sample converted (X) at any time, t, was calculated following Eq. 4.2.3:

$$X = \frac{m_i - m_t}{m_i - m_f} \tag{4.2.3}$$

where m_i is the initial mass, m_t is the mass at any time, t, and m_f is the final mass after the hold at 950 ℃. Derivative thermogravimetric curves were plotted as dX/dt $\left(s^{-1}\right)$ versus temperature. DSC data was normalized as heat flow per sample mass at any given instant (m_t). DTG curves are compared to those from an in-house sample of Illinois No. 6 coal, a high volatile bituminous coal from the Illinois # 6 (Herrin) seam from the Argonne Premium Coal Bank. Dewaterability was also determined by measuring the Capillary Suction Time (CST) in order to assess the improvement of sludge dewaterability developed by HTC process. CST was measured using a capillary suction timer type 304B manufactured by Triton Electronics Ltd. The CST tester was used to measure the time required for water separated from sludge to travel a certain distance through a filter paper (Whatman 17 CHR). The test provides a quantitative measure (in seconds) of how readily sludge releases water. CST analyses were carried out according to the Standard Methods (APHA 2012). The liquid phase was characterized by measuring pH, COD, organic nitrogen, ammonia nitrogen, phosphorous and metals as described above. Moreover, measurement of RBCOD were performed following the procedure described in Andreottola et al. (2002) to measure NH_4^+ nitrogen and soluble COD, samples were screened through a 0.45 μm filter.

4.3 Result and Discussion

To assess the optimal point to withdraw sludge from the treatment process for hydrothermal carbonization, three samples were pulled from various points along the process: Thickened, Digested, and Dewatered. The feedstocks characteristics are presented in Table 4.1.

Table 4.1: feedstock characteristics of thickened, digested, and dewatered sludge.

Analysis	Thickened Sludge	Digested Sludge	Dewatered Sludge
Moisture Content[ar] [wt %]	97,1 ± 0,1	97,1 ± 0,3	74,9 ± 0,1
Total Solids [g L^{-1}]	29,1 ± 0,4	29,0 ± 2,3	n.a.[b]
Fixed + Volatile Solids [g L^{-1}]	26,7 ± 0,4	15,4 ± 0,9	n.a.[b]
Total Solids [%]	2,9 ± 0,0	2,9 ± 0,0	25,1 ± 0,1
Fixed + Volatile Solids [% of Total Solids]	91,8 ± 2,6	53,1 ± 7,3	74,1 ± 0,1
Total COD [gCOD L^{-1}]	28,0 ± 1,0	18,0 ± 1,0	1,2 ± 0.06[a]
Soluble COD [gCOD L^{-1}]	2,3 ± 0,1	0,4 ± 0,1	0,3 ± 0.01[a]
Organic Nitrogen [gN-N_{org} L^{-1}]	0,47 ± 0,23	1,29 ± 0,07	0,07 ± 0.00[a]
Ammonia Nitrogen [gN-NH_4^+ L^{-1}]	0,49 ± 0,01	0,88 ± 0,01	0,00 ± 0.00[a]
Total Phosphorous [mg P L^{-1}]	175 ± 9	187 ± 9	10 ± 1[a]
pH	6,87 ± 0,01	7,39 ± 0,01	n.a.[c]
Ultimate Analysis (dry basis)			
C [wt %]	45,96 ± 0,20	25,6 ± 0,33	35,91 ± 0,25
H [wt %]	6,57 ± 0,02	3,96 ± 0,06	5,42 ± 0,01
N [wt %]	4,26 ± 0,01	3,59 ± 0,10	5,81 ± 0,02
S [wt %]	0,64 ± 0,02	0,71 ± 0,03	0,91 ± 0,12
O [wt %][(by difference)]	27,61 ± 4,86	21,16 ± 0,79	23,52 ± 0,52
Proximate Analysis (dry basis)			
Fixed Carbon [wt %]	12,60 ± 1,40	4,76 ± 3,78	5,90 ± 0,62
Volatile Matter [wt %]	72,50 ± 3,20	50,25 ± 3,51	65,67 ± 0,50
ASH [wt %]	14,96 ± 4,62	44,99 ± 0,27	29,43 ± 0,13
Heat Content			
HHV [MJ $kg^{-1}_{dry\ feedstock}$]	20,50 ± 0,14	10,61 ± 1,79	16,02 ± 0,09

[ar] as received
[a] Based on 1g of dry biomass dissolved in one litre of distilled water
[b] dewatered sludge it is solid, so it's not possible to express the concentration in g L^{-1}
[c] pH meter is only for liquid waste

4.3.1 Product Distribution and Characterization as a Function of Sludge Type and Treatment

Solid hydrochar yields are strongly influenced by both sewage sludge feedstock and HTC temperature and residence time, as shown in Table 4.2.

In Figure 4.2 a) gas yield of all the kinds of sludge computed with the ideal gas law (and hypothesis of all CO_2) are reported. The lowest yield was obtained with dewatered sludge obviously at 190 ℃ and 30min, while the highest at 250 ℃ and 60 *min* with digested sludge. The gas yield is low; it can vary between the 2 and 8 % as a function of the kind of sludge and increasing with temperature and residence time. Figure 4.2 b) shows hydrochar yield for all the performed tests and kind of sludge. Concerning thickened sludge, hydrochar yield, with 30 minutes of residence time, varies from 0.77 at 190 ℃ to 0.49 at 250 ℃, while, with 60 minutes of residence time, it varies from 0.67 at 190 ℃ to 0.52 at 250 ℃. As expected from literature, hydrochar yield decreases with temperature and residence times. Regarding digested sludge, hydrochar yield, with 30 minutes of residence time, varies from 0.83 at 190 ℃ to 0.65 at 220 ℃, while, with 60 minutes of residence time, it varies from 0.82 at 190 ℃ to 0.65 at 250 ℃. The digested sludge has more scattered data in comparison with thickened sludge, but, in general, the hydrochar yield decreases with temperature and residence time. Concerning dewatered sludge, hydrochar yield, with 30 minutes of residence time, varies from 0.88 at 190 ℃ to 0.68 at 250 ℃, while, with 60 minutes of residence time, it varies from 0.86 at 190 ℃ to 0.67 at 250 ℃. The dewatered sludge show a very good reproducibility of data in comparison with thickened and digested sludge. For dewatered sludge, the residence time does not seem to affect hydrochar yield. As expected as a result of the carbonization

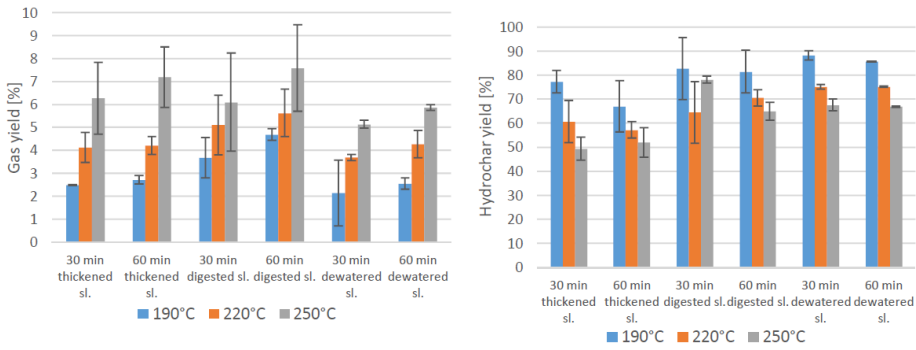

Figure 4.2: product distribution from hydrothermal carbonization of thickened, digested, and dewatered sludge.

process, which liberates organics from the solid matrix and forces them

Table 4.2: process yields and product characteristics of hydrothermal carbonization of thickened, digested, and dewatered sludge.

Property	HTC Temp [°C]	Thickened Sludge		Digested Sludge		Dewatered Sludge	
		30 min. HTC	60 min. HTC	30 min. HTC	60 min. HTC	30 min. HTC	60 min. HTC
Solid Yield [wt%]	190	77,2 ± 4,7	67,0 ± 11	82,8 ± 82,8	81,5 ± 8,9	88,2 ± 2,0	85,6 ± 0,0
	220	60,6 ± 8,8	57,2 ± 3,4	64,6 ± 64,6	70,6 ± 3,4	75,1 ± 1,0	75,2 ± 0,3
	250	49,4 ± 4,8	52,0 ± 6,2	78,1 ± 78,1	64,9 ± 3,7	67,6 ± 2,5	66,8 ± 0,2
Gas Yield [wt%]	190	2,5 ± 0,0	2,7 ± 0,2	3,7 ± 0,9	4,7 ± 0,3	2,1 ± 1,4	2,6 ± 0,2
	220	4,1 ± 0,7	4,2 ± 0,4	5,1 ± 1,3	5,6 ± 1,0	3,7 ± 0,1	4,3 ± 0,6
	250	6,3 ± 1,6	7,2 ± 1,3	6,1 ± 2,1	7,6 ± 1,9	5,1 ± 0,2	5,9 ± 0,1
Liquid Yield [wt%]	190	20,3 ± 2,4	34,9 ± 5,4	43,2 ± 41,8	43,1 ± 4,6	45,2 ± 1,7	44,1 ± 0,1
	220	35,3 ± 4,7	30,7 ± 1,9	34,8 ± 32,9	38,1 ± 2,2	39,4 ± 0,6	39,7 ± 0,4
	250	44,3 ± 3,2	29,6 ± 3,8	42,1 ± 40,1	36,3 ± 2,8	36,4 ± 1,3	36,4 ± 0,2
Total COD [g L^{-1}]	Raw	28,1 ± 1,4	28,1 ± 1,4	18,0 ± 0,9	18,0 ± 0,9	193,2 ± 30,0	193,2 ± 30,0
	190	14,1 ± 2,0	15,3 ± 0,7	9,1 ± 0,2	9,3 ± 0,4	55,3 ± 0,3	56,3 ± 2,8
	220	15,4 ± 1,4	15,1 ± 1,1	11,3 ± 1,2	9,9 ± 0,1	56,7 ± 1,4	54,1 ± 2,7
	250	18,4 ± 0,7	18,4 ± 1,8	10,4 ± 0,7	8,8 ± 0,4	64,9 ± 8,2	57,5 ± 0,3
Soluble COD [g L^{-1}]	Raw	2,3 ± 0,1	2,3 ± 0,1	0,4 ± 0,0	0,4 ± 0,0	47,2 ± 2,4	47,2 ± 2,4
	190	10,5 ± 1,0	13,4 ± 0,4	6,4 ± 0,3	6,7 ± 0,5	49,8 ± 0,4	55,1 ± 2,8
	220	11,9 ± 1,5	13,5 ± 0,5	6,7 ± 0,3	6,7 ± 0,5	44,8 ± 3,4	45,7 ± 5,5
	250	15,3 ± 0,9	13,7 ± 0,1	8,3 ± 0,8	5,7 ± 0,2	57,5 ± 9,8	46,8 ± 0,6
pH	Raw	6,87 ± 0,01	6,87 ± 0,01	7,39 ± 0,01	7,39 ± 0,01	n.a.[a]	n.a.[a]
	190	5,07 ± 0,01	5,07 ± 0,01	8,04 ± 0,21	7,79 ± 0,02	7,09 ± 0,07	7,30 ± 0,07
	220	5,07 ± 0,01	5,15 ± 0	7,77 ± 0,02	7,74 ± 0,07	7,50 ± 0,01	7,77 ± 0,01
	250	5,41 ± 0,07	5,68 ± 0	7,79 ± 0,56	8,22 ± 0,14	8,08 ± 0,04	8,03 ± 0,05
Total Phosphorous in Liquid [mg L^{-1}]	Raw	175,00 ± 9,00	175,00 ± 9,00	187,00 ± 9,00	187,00 ± 9,00	10,00 ± 1,00	10,00 ± 1,00
	190	32,45 ± 0,11	38,40 ± 0,09	19,60 ± 0,30	22,73 ± 0,05	0,34 ± 0,00	0,37 ± 0,00
	220	20,20 ± 0,07	16,35 ± 0,22	19,75 ± 0,29	17,80 ± 0,09	0,23 ± 0,00	0,22 ± 0,00
	250	16,13 ± 0,09	11,10 ± 0,15	19,27 ± 0,29	12,15 ± 0,07	0,19 ± 0,00	0,17 ± 0,00
Total Phosphorous in Solid [mg g^{-1}]	Raw	5,22 ± 0,10	5,22 ± 0,10	5,81 ± 0,13	5,81 ± 0,13	9,22 ± 0,33	9,22 ± 0,33
	190	6,21 ± 0,74	6,79 ± 0,39	7,22 ± 0,69	7,40 ± 1,42	9,23 ± 0,49	9,37 ± 0,36
	220	7,81 ± 0,33	9,36 ± 0,17	7,50 ± 0,47	7,47 ± 1,47	10,46 ± 0,18	10,58 ± 0,23
	250	9,90 ± 0,47	10,15 ± 4,60	7,35 ± 0,94	6,67 ± 1,20	10,83 ± 0,77	10,94 ± 0,87
Organic Nitrogen in Liquid [g L^{-1}]	Raw	0,470 ± 0,230	0,470 ± 0,230	1,290 ± 0,070	1,290 ± 0,070	11,023 ± 0,000	11,023 ± 0,000
	190	0,075 ± 0,003	0,076 ± 0,001	1,305 ± 0,011	1,228 ± 0,030	4,456 ± 0,977	4,124 ± 0,206
	220	0,084 ± 0,008	0,066 ± 0,004	1,371 ± 0,011	0,880 ± 0,002	2,372 ± 0,614	1,547 ± 0,119
	250	0,090 ± 0,006	0,085 ± 0,003	1,297 ± 0,011	1,511 ± 0,016	1,674 ± 0,303	1,422 ± 0,745
Ammonia Nitrogen in Liquid [g L^{-1}]	Raw	0,490 ± 0,010	0,490 ± 0,010	0,880 ± 0,010	0,880 ± 0,010	0,598 ± 0,000	0,598 ± 0,000
	190	0,357 ± 0,001	0,553 ± 0,000	0,678 ± 0,001	0,717 ± 0,004	2,748 ± 0,124	3,800 ± 0,190
	220	0,423 ± 0,001	0,501 ± 0,000	0,762 ± 0,001	1,040 ± 0,000	4,421 ± 0,313	4,566 ± 0,610
	250	0,584 ± 0,001	0,592 ± 0,000	0,973 ± 0,001	0,802 ± 0,002	6,866 ± 0,436	6,507 ± 0,407

[a] pH meter is only for liquid waste

into the water phase while generating CO_2 upon further oxidation, the Total COD present decreased as carbonization severity (time, temperature) increased for all three sludge samples, while soluble COD increased with increasing severity. Such behaviour has been noted in the literature for other biomasses, including sludge, secondary sludge, wood waste and dairy waste (Jomaa et al. 2003). The decrease in pH for increasingly severe carbonization of the thickened sludge is not surprising; volatile fatty acids (VFAs) present in primary sludge, especially acetic acid, are known to remain stable in the liquid phase, only breaking down at higher carbonization temperatures (Jomaa et al. 2003). Here we find that the pH for the thickened sludge drops from 6.9 to 5.1 for both the 190 and 220 ℃ conditions, and rises to 5.4 and 5.7 for the 30 min and 60 min 250℃, respectively. This suggests that the HTC was able to hydrolyse the VFAs at higher temperatures, reducing the acid content. For secondary sludge, the pH increases slightly with increasing carbonization, but is higher to begin with, suggesting that the acidic content was lowered by the anaerobic digestion steps. This data, combined with the increased gas yields as temperature and time increase, support the idea that the hydrothermal decomposition overall proceeds via a hydrolysis then oxidation to CO_2 pathway.

4.3.2 Distribution of Phosphorous and Nitrogen: Potential for Use as Soil Amendment

The total P concentrates in the solid hydrochar (all samples/processing conditions) suggests its potential for use as a soil amendment. Given the decrease in organic nitrogen in the solid for the thickened sludge, and the increase in organic nitrogen for both digested and dewatered sludge (at all processing conditions), the post-digested sludge samples are likely better candidates for soil amendments. For thermally treated (pyrolysis, gasification, incineration) sludge samples, it was found that higher P fertilizer values are a function of various mechanisms, including structural surface changes, and improved association of P to inorganics such as Mg, Ca, and Al (Thomsen et al. 2017). In addition to phosphorus, as reported in Figure 4.3, in all sample several mg of other nutrients, such as K, Na, Ca and Mg, were measured, promoting hydrochar as soil improver. While soil incubation studies are beyond the scope of the present work, prior work by Thomsen et al. (2017) suggests that the more heavily oxidized hydrochar samples (e.g. those that released more CO_2 and thus had higher gas yield) containing more Mg, Ca and Al would have a higher P availability (Thomsen et al. 2017). This corresponds to the digested 250 ℃, 60 min and dewatered 220 and 250 ℃, 30 and 60 min samples. Possible explanations include a higher surface area for enhanced

transport of P and also the formation of Mg-P mineral complexes (Adam et al. 2009), which if the samples were further heated would crystallize to species such as farringtonite and stanfieldite. Further work will investigate the degree to which oxidation plays a role in P plant availability, as well as the impact of HTC processing conditions itself on the volatilization and re-condensation of P species on the hydrochar surfaces. In the end, the initial concentration of heavy metal is a limiting factor on the final use/disposal of hydrochar: many heavy metals (As, Cd, Cr, etc.) do not vary their concentration during the process or tend to precipitate, but for the use as soil improver the hydrochar has to respect the values reported in Table 1.5 in the Chapter 1. In this work, for all samples/processing conditions the limits are respected for As, Cd, Cr, Co, Pb, Hg and Ni, while for Cu and Zn the limits are respected for all the kind of sludge at 190 ℃, while for the samples treate at 220 and 250 ℃, Cu and Zn concentrations are above the limits.

4.3.3 Energy Yield and Oxidative Reactivity: Potential for Use as Solid Fuel

In Table 4.3 are reported the solid fuel characteristics of hydrochar from thickened, digested, and dewatered sludge: Figure 4.4 b) shows the HHV of hydrochar for all the performed tests and kind of sludge. For all the runs, except for thickened sludge at 190 ℃and 60 minutes and dewatered sludge at 190 ℃and 30 minutes, the HHV of hydrochar results lower than the corresponding HHV of the raw sludge, so instead to have an energy densification, the hydrochar losses calorific value. As it can be observed in Table 4.3, Carbon fraction of hydrochar is negatively affected by the process, while ASH content increases dramatically, so lower HHV values are thus explained. Regarding the two exceptions, C fraction slightly increased, but the ASH content raised too, so energy densification was limited. In Figure 4.4 a), Van Krevelen's diagram is reported. Empty indicators are initial feedstocks, while different colours mean different operative conditions. Circles are for thickened sludge, squares are for digested sludge and rhombus are for dewatered sludge. It is possible to observe that for thickened and dewatered sludge H/C and O/C decrease so dehydration and decarboxylation occur as expected. Concerning digested sludge, H/C decreases while O/C increase, so dehydration occurs while, instead of decarboxylation, demethylation occurs. In Funke and Ziegler (2010) is stated that demethylation can occurs during hydrothermal carbonisation. Figure 4.5 plots the DTG curves of the hydrochar samples produced at each of the three carbonization temperatures at 30 minutes alongside an Illinois No. 6 coal sample. As can be seen, the hydrochar sludge samples are considerably more reactive than the

Table 4.3: analysis of solid fuel characteristics of hydrochars from thickened, digested, and dewatered sludge.

Property	HTC Temp [°C]	Thickened Sludge		Digested Sludge		Dewatered Sludge	
		30 min. HTC	60 min. HTC	30 min. HTC	60 min. HTC	30 min. HTC	60 min. HTC
Ultimate Analysis (dry basis)							
C [wt%]	Raw	45,96 ± 0,20	45,96 ± 0,20	25,60 ± 0,33	25,60 ± 0,33	35,91 ± 0,25	35,91 ± 0,25
	190	44,56 ± 0,39	46,11 ± 0,39	19,22 ± 1,37	14,16 ± 2,57	36,61 ± 0,02	35,07 ± 0,23
	220	44,86 ± 0,51	43,15 ± 0,19	11,70 ± 0,64	10,21 ± 0,58	35,19 ± 0,17	35,75 ± 0,31
	250	41,68 ± 0,29	41,21 ± 0,52	12,51 ± 0,26	12,02 ± 0,05	35,30 ± 0,18	35,57 ± 0,08
H [wt%]	Raw	6,57 ± 0,02	6,57 ± 0,02	3,96 ± 0,06	3,96 ± 0,06	5,42 ± 0,00	5,42 ± 0,00
	190	6,24 ± 0,08	6,46 ± 0,06	2,63 ± 0,16	2,00 ± 0,29	4,92 ± 0,02	4,61 ± 0,03
	220	5,95 ± 0,01	5,69 ± 0,02	1,61 ± 0,08	1,37 ± 0,07	4,32 ± 0,01	4,36 ± 0,03
	250	5,03 ± 0,05	5,01 ± 0,03	1,65 ± 0,01	1,56 ± 0,02	4,11 ± 0,00	4,05 ± 0,01
N [wt%]	Raw	4,26 ± 0,00	4,26 ± 0,00	3,59 ± 0,10	3,59 ± 0,10	5,81 ± 0,02	5,81 ± 0,02
	190	2,23 ± 0,07	2,10 ± 0,07	1,58 ± 0,07	1,07 ± 0,17	4,27 ± 0,06	3,95 ± 0,01
	220	1,87 ± 0,24	1,86 ± 0,07	0,80 ± 0,08	0,66 ± 0,01	3,48 ± 0,02	3,45 ± 0,02
	250	1,89 ± 0,05	1,99 ± 0,04	0,70 ± 0,00	0,69 ± 0,02	3,16 ± 0,04	3,12 ± 0,02
O [wt%]	Raw	27,61 ± 4,86	27,61 ± 4,86	21,16 ± 0,79	21,16 ± 0,79	23,52 ± 0,52	23,52 ± 0,52
	190	28,52 ± 6,69	25,97 ± 4,63	18,43 ± 3,50	15,67 ± 6,89	18,55 ± 0,17	19,33 ± 0,58
	220	25,51 ± 6,34	26,43 ± 5,06	12,35 ± 1,03	18,93 ± 1,10	16,53 ± 0,33	15,34 ± 0,49
	250	22,47 ± 6,44	21,59 ± 3,83	11,72 ± 2,00	7,17 ± 2,53	14,07 ± 0,44	14,12 ± 2,18
Proximate Analysis (dry basis)							
Fixed Carbon [wt%]	Raw	12,56 ± 1,43	12,56 ± 1,43	4,76 ± 3,78	4,76 ± 3,78	5,90 ± 0,62	5,90 ± 0,62
	190	4,25 ± 2,50	4,58 ± 1,75	1,70 ± 0,09	2,06 ± 0,34	5,37 ± 0,23	9,94 ± 6,93
	220	5,37 ± 4,00	5,23 ± 3,97	1,26 ± 0,07	0,13 ± 0,01	4,04 ± 2,06	9,83 ± 5,58
	250	5,31 ± 5,85	6,12 ± 5,93	0,62 ± 0,05	1,38 ± 0,09	6,27 ± 0,61	7,02 ± 0,03
Volatile Matter [wt%]	Raw	72,48 ± 3,19	72,48 ± 3,19	50,25 ± 3,51	50,25 ± 3,51	65,67 ± 0,50	65,67 ± 0,50
	190	70,84 ± 6,65	71,03 ± 5,36	41,09 ± 3,22	30,84 ± 4,20	58,98 ± 0,29	53,02 ± 6,61
	220	66,05 ± 5,56	63,57 ± 7,81	26,17 ± 1,59	31,99 ± 0,90	55,48 ± 2,19	49,07 ± 5,72
	250	60,06 ± 2,19	56,70 ± 3,95	25,97 ± 1,68	21,65 ± 4,68	50,37 ± 0,39	49,85 ± 2,03
Ash (Inorganic) [wt%]	Raw	14,96 ± 2,31	14,96 ± 2,31	44,99 ± 3,65	44,99 ± 3,65	28,43 ± 0,56	28,43 ± 0,56
	190	24,91 ± 4,57	24,40 ± 3,56	57,21 ± 1,61	67,10 ± 2,27	35,66 ± 0,26	37,05 ± 6,77
	220	28,58 ± 4,78	31,20 ± 5,89	72,57 ± 0,80	67,88 ± 0,45	40,48 ± 2,13	41,10 ± 5,65
	250	34,63 ± 4,02	37,18 ± 4,94	73,42 ± 0,86	76,97 ± 2,34	43,36 ± 0,50	43,14 ± 1,03
Combustion Analysis							
HHV [MJ kg^{-1}]	Raw	20,50 ± 0,14	20,50 ± 0,14	10,66 ± 1,79	10,66 ± 1,79	16,02 ± 0,09	16,02 ± 0,09
	190	19,45 ± 0,64	20,71 ± 0,03	9,27 ± 1,73	7,97 ± 1,77	16,30 ± 0,19	15,96 ± 0,07
	220	20,06 ± 0,90	18,72 ± 0,03	8,96 ± 1,77	7,86 ± 0,39	15,70 ± 0,09	15,47 ± 0,37
	250	18,66 ± 0,26	19,17 ± 0,61	8,59 ± 1,78	9,37 ± 1,39	15,98 ± 0,11	15,33 ± 0,26

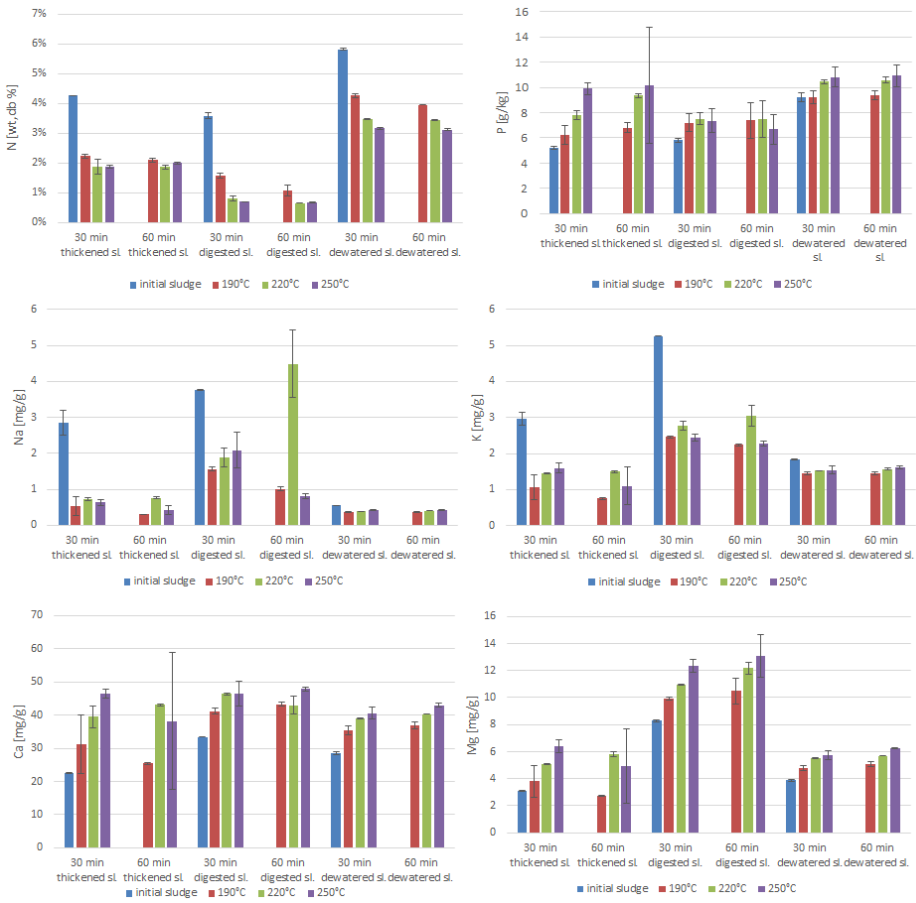

Figure 4.3: nutrient product balance resulting from hydrothermal carbonization of thickened, digested, and dewatered sludge.

coal sample. Their peak DTG temperatures (highest conversation rates) occur hundreds of degrees less than the coal sample, and at half the conversion rate. The highest peak mass loss rates occur for all three hydrochars produced from the thickened sludge, prior to any anaerobic digestion. Post-digestion, which the shape of the DTG curves changes, the peak rates are quite similar for both the thickened and dewatered sludge. For all three samples, the 190 °Ccarbonized hydrochars display the highest reactivity compared to the other HTC temperatures. Especially at such mild conditions, HTC does not significantly carbonize the sample – oftentimes the original materials' microstructure is preserved, whereas higher temperatures lead to a more complete destruction of the carbon matrix (Kruse et al. 2013; Titirici et al. 2008; Volpe and Fiori 2017). Given the relatively high reactivity of the sludge hydrochars, it

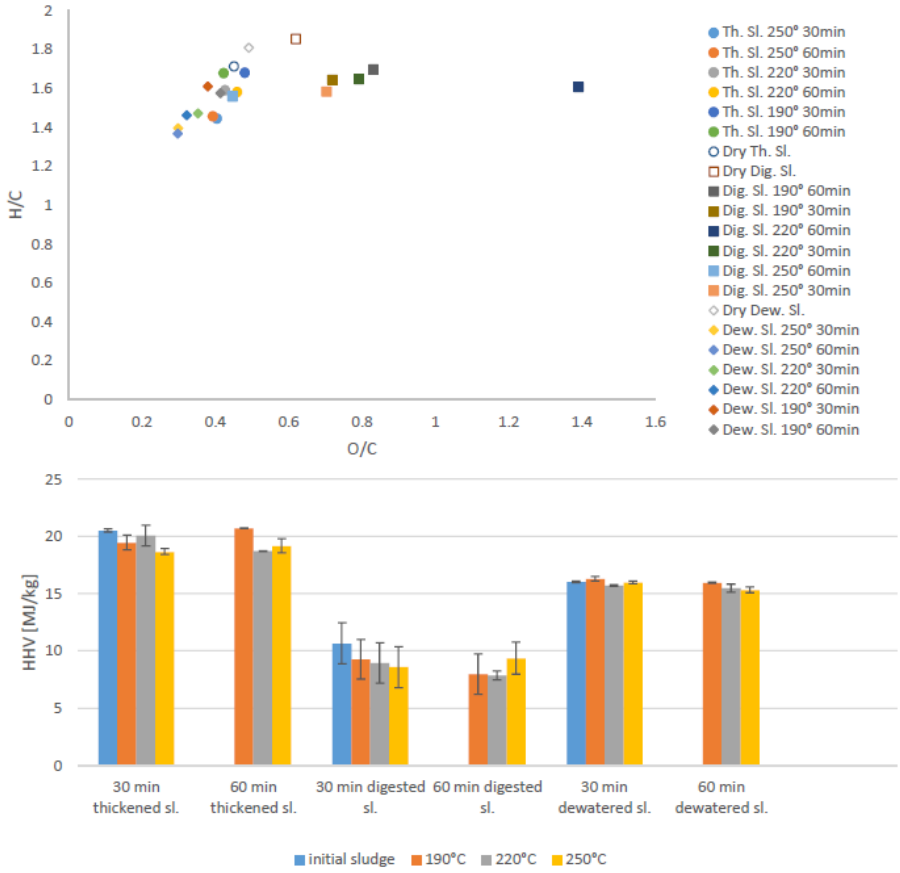

Figure 4.4: energetic considerations [a) van Krevelen, b) HHV].

may be difficult to combust them for electricity generation in current boilers designed for solid fuels such as coal. While the higher heating values of especially thickened sludge (18-21 $MJ\ kg^{-1}$) are suitable for such combustion schemes, their lower ignition and peak reactivity temperatures are considerably lower than that of most bituminuous coals, and therefore may lead to loss of efficiency in boilers (Khan et al. 2009). That, combined with the higher ash content that could result in slagging and fouling, suggest that the sludge hydrochars may perform better in co-combustion scenarios (Haykiri-Acma et al. 2015). Our group has demonstrated that blending biofuels with similar characteristics at ratios less than 20 wt % with coal mitigates fuel segregation and efficiency loss issues while increasing the share of renewables in energy generation portfolios (Xue et al. 2018; Goldfarb and Liu 2013; Celaya et al. 2015). Recent work in the literature suggests that hydrochars can be co-combusted with a variety of coals in economically, environmentally and energetically vi-

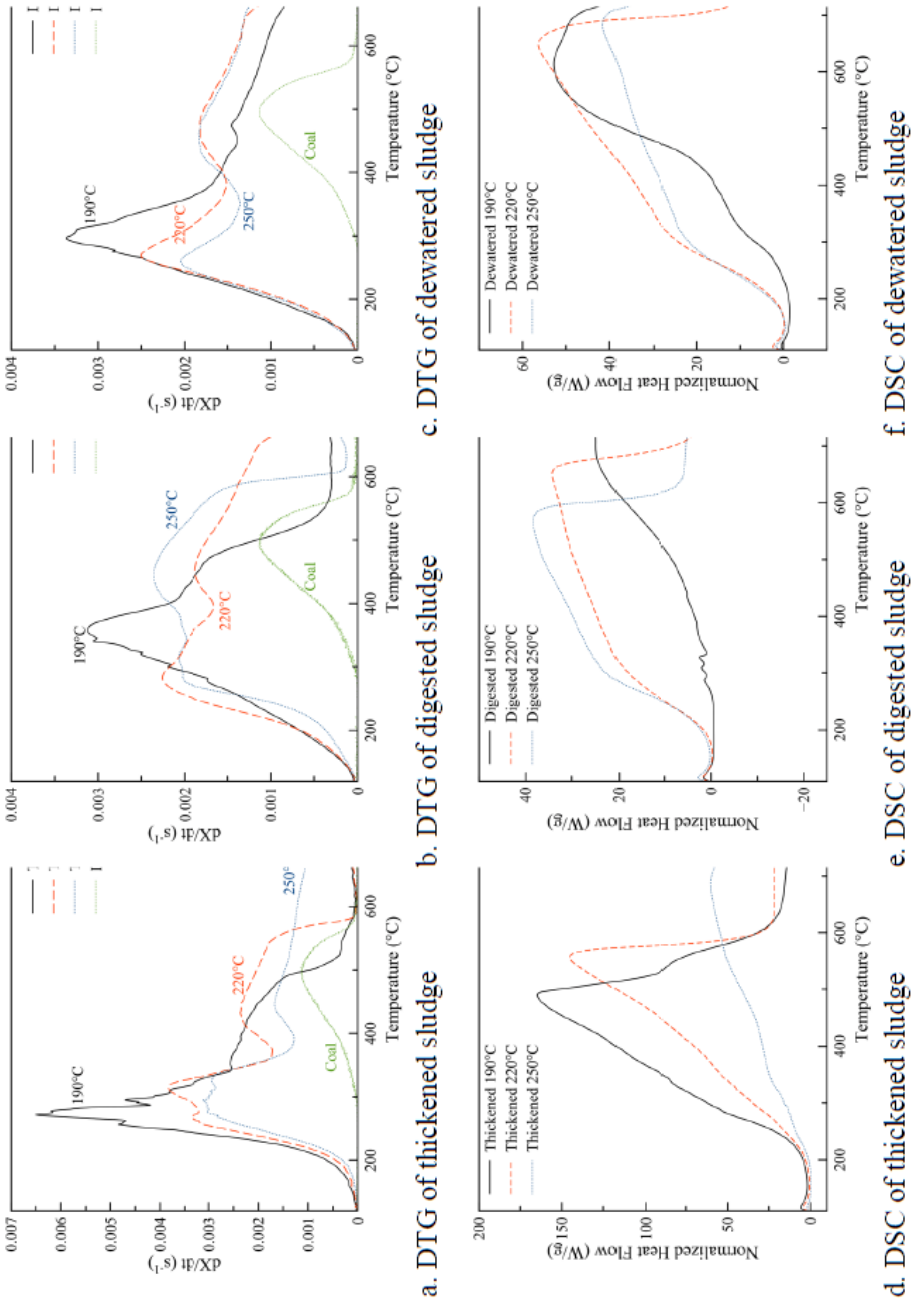

Figure 4.5: thermal analysis of oxidation at 10° ℃ min^{-1} of selected sludge samples carbonized for 30 minutes at the given temperature, DTG compared to oxidation of IL. No. 6 Coal.

able schemes in existing infrastructure (Cartmell et al. 2006; Xiao et al. 2010; Otero et al. 2008; Stasta et al. 2006), and may even improve the emissions profile at optimized blending ratios (Parshetti et al. 2013).

4.3.4 Dewaterability

Figure 4.6 reports the effect of HTC process on sludge dewaterability: for raw dewatered sludge, after 60 *min*, CST wasn't completed, while after HTC treatment at 190 ℃ and 60 *min* the CST was completed after 380 *s*. Increasing HTC temperature, CST was 209 *s* at 220 ℃ and, in the end, 90 *s* after HTC performed at 250 ℃. The improved dewaterability affects strongly the economics of the sludge disposal because HTC can reduce the volume of sludge to dispose of up to four times and not below three times.

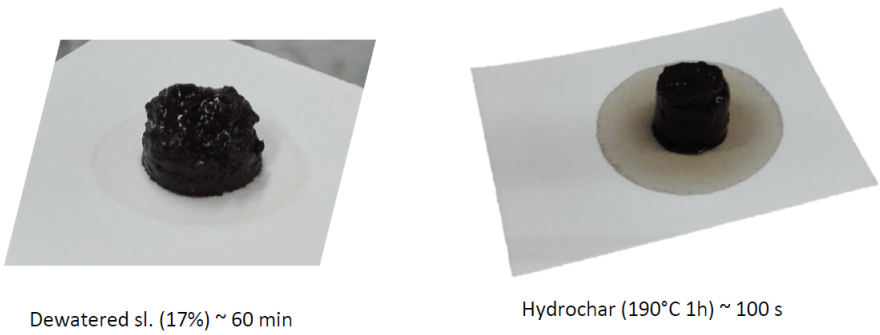

Figure 4.6: sludge and hydrochar dewaterability.

4.3.5 Further Considerations

While there is considerable potential to use HTC to convert primary and secondary sludges to renewable fuels, and/or use the hydrochars for nutrient recovery redistribution, there remains several unanswered questions about the feasibility of implementing such a process. One question is what to do with the process water remaining after treatment. While this is beyond the scope of the present work, others have previously demonstrated several potential management options. Process liquors remaining after hydrothermal treatments have been shown to be suitable feedstocks for aerobic, anoxic and anaerobic processes (Barlindhaug and Ødegaard 1996; Friedman et al. 1988; Wirth et al. 2015). Our experimental data testify that RBCOD, namely readily biodegradable COD, for HTC performed at 190 ℃, reached values above 85 % of total COD, while increasing temperature led to value below 15 % at 250 ℃. While wet air oxidation

liquors have shown some inhibitory behaviors for strictly anaerobic treatments (Friedman et al. 1988), this has not been the case for HTC liquors (Aragón-Briceño et al. 2017; Wirth et al. 2015; Wirth and Mumme 2013). As demonstrated by Qiao et al. (2011), HTC process water may actually increase the efficiency of the solid hydrolysis step (Qiao et al. 2011), a rate-limiting step in the digestion process (Appels et al. 2008; Vavilin et al. 1996) and enhance methane production in the digester (Nuchdang et al. 2018). Second, the fate of some heavy metals during HTC, especially Cu and Cr, may complicate the use of these materials as a soil amendment, as successive WWT and carbonization concentrates them within the hydrochar. Shi et al. (2014) demonstrated that cadmium in sludge hydrochars can be immobilized by the synergistic nature of apatite P present in the chars and addition of hydroxyapatite (Shi et al. 2014). However, as both acid and alkaline leaching have been shown to dissolve phosphate in sludges and sludge ashes (Stark et al. 2006), the long-term stability of the Cd immobilized by the method of hydroxyapatite addition is not clear. Prior work by Yoshizaki and Tomida (2000) demonstrated that such heavy metals could be removed by phosphoric acid and hydrogen peroxide for downstream reuse and recovery (Yoshizaki and Tomida 2000). Their method had enhanced recovery and was more environmentally and economically viable than treatment with hydrochloric acid or sulfuric acid, opening a potential pathway for extraction of the metals from hydrochars. Such treatment would likely act as a porogen to increase the surface area of the hydrochars (Hotová et al. 2018), increasing their ability to retain water and slow-release nutrients when used as a solid amendment (Liang et al. 2006) and open up possibilities for conversion of the materials to activated carbons for use in water treatment, battery electrodes, and other high-value materials (Goldfarb et al. 2017b; Goldfarb et al. 2017a; Işıtan et al. 2016) .

4.4 Conclusions

Hydrothermal Carbonization (HTC) process was performed to convert different kinds of sludge into hydrochar at 190, 220 and 250 ℃ with different residence time of 30 min and 60 min in a batch lab-scale stainless steel reactor. HTC process allows sludge reduction (yield of hydrochars were 49-89 % in function of temperature, residence time and kind of sludge) and typically increases the energy content in the hydrochar but due to an increment in ash content that reached values above 70 %, the HHV of hydrochar from sludge slightly decrease (HHVs of hydrochars were 0.74-1.02 times of initial feestocks). The low ignition and peak reactivity temperatures combined with the high ash content of hydrochar

suggest that the sludge hydrochars may perform better in co-combustion scenarios. The gas yields were low; it can vary between the 2 and 8 % as a function of the kind of sludge and increasing with temperature and residence time. The HTC of sludge seems to precipitate the phosphorus from the liquid phase to the solid phase (only the 2-22 % of phosphorus remains in the liquid phase), ICP analysis confirms this. The resulting hydrochars have: Mg, Na, K and Ca content of several $g\ kg^{-1}$ and Pb, Cd, Ni, Zn, Cu, Hg, Cr, As and Co content of the order of $mg\ kg^{-1}$: HTC process tends to concentrate P, Mg and Ca and reduce K and Na content in the hydrochar in respect to the initial dry sludge, so hydrochar could be a candidate as soil amendments, but further studies are required. HTC improves dewaterability of sludge, reducing dramatically CST that measures the resistance to release water,allowing the reduction of sludge to dispose of. In the end, further research are required on the HTC process water in order to valorize it for biogas production.

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Chapter 5

Anaerobic Biodegradability of Hydrothermal Converted Sewage Sludge

This Chapter is a description of the system designed in order to perform Bio Methane Potential tests: some preliminary test on sewage sludge traded by means of hydrothermal process are reported. This Chapter is a pre-step for a future experimental work on the biogas production from the HTC process work, a natural consequence of the Chapters 2 and 4.

Anaerobic Biodegradability of Hydrothermal Converted Sewage Sludge

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5.0 Abstract

Anaerobic digestion is a biological process in which, in the absence of oxygen, the organic matter is degraded by anaerobic bacteria. Within a wastewater treatment plant the anaerobic digestion takes place in the sludge line where the stabilization of the sludge produced in the water line is carried out. Mainly, the substrate transformation by AD is composed by four successive stages as reported in Chapter 2: Hydrolysis, Acidogenesis or fermentation, Acetogenesis and Methanogenesis. The hydrolysis step is generally the limiting step, so the aim of this work is to study

hydrothermal conversion applied to sewage sludge in order to ehnance this limiting step.

5.1 Introduction

Sludge production within wastewater treatment plants accounts for a very small proportion (about 1 %) of the total volume of treated wastewater, while the processes used for its treatment and disposal account for between 20 % and 60 % of the plant's total operating costs. Anaerobic Digestion allows the reduction of the amount of final sludge to dispose of (allowing a reduction of about 50 % of the volatile solids present in the digestate), and ensuring the production of a new source of energy (biogas), which can be used for energy recovery. In order to increase the efficiency of anaerobic digestion and reduce the amount of sludge to dispose of, various strategies have been proposed. In particular, it has been observed that by introducing pre-treatments (of different nature) upstream anaerobic digestion, an improvement of the process is observed, due to an increase of hydrolysis rate step, which normally is the limiting reaction. One of the most promising is the hydrothermal conversion in the "field" of thermal hydrolysis, where thickened sludge is heated up to 120 -170 ℃ at vapour pressure (2-8 bar), improving sludge dewatering and maximizing biogas production in anaerobic digesters. In many studies, thermal hydrolysis is a pre-treatment of anaerobic digestion in order to maximize biogas production and energy exploitation: Li and Noike (1992) stated that the optimal parameters are 170 ℃and 60 min as above 180 ℃the degree of solubilisation increases but unbiodegradable compounds begin to synthesize. Kepp et al. (2000) reported results from the first thermal hydrolysis full-scale plant. The authors stated that the best sludges to apply thermal hydrolysis are municipal and industrial waste activated sludge. The authors also found that thermal hydrolysis reduces anaerobic digesters volume up to 50 % and increase net electricity production up to 20 % due to improvement of biogas production. Donoso-Bravo et al. (2011) investigated the effect of different residence times (5-30 min) on carbohydrates, proteins and VFAs with a Lab-scale system (V=0.5 L) and a Pilot-scale system (V=20 L). The authors showed that the residence time does not influence the degree of solubilisation of proteins and carbohydrates and the total biogas production, but it has more influence on the maximum biogas production rate. Both Kepp et al. (2000) and Donoso-Bravo et al. (2011) showed that thermal hydrolysis improves sludge dewatering and degree of sterilization (no pathogens were detected). High degrees of sterilization are important to allow sludge to be used in agriculture after composting and thus landfill-

ing and incineration are avoided. In order to improve energy exploitation, Shana et al. (2013) investigated the effect of thermal hydrolysis applied to digested sludge. The authors focused their studies on carbohydrate biodegradation kinetics in anaerobic biodegradability tests and found an improvement in biogas production in the configuration anaerobic digestion+thermal hydrolysis+anaerobic digestion compared to the configuration thermal hydrolysis+anaerobic digestion. The aim of this work is to develop a BMP system in order to apply hydrothermal conversion upstream of anaerobic digestion of sewage sludge and measure the enhancement of biogas production. Previous studies have already demonstrated the effectiveness of this technology: in particular, it has been observed that applying hydrothermal treatments to sludge favours the breakdown of sludge structure and the breaking of the cell walls, so more organic compounds are easily subject to anaerobic conversion.

5.2 Material and Methods

Dynamic thickened Secondary Sludge was collected from the municipal wastewater treatment plant (WWTP) of Trento, Italy, which uses a Conventional Activated Sludge (CAS) and Membrane BioReactor (MBR) system. The secondary sludge coming from the CAS system is sent to a dynamic thickener (Pipe 2 of Figure 5.1). Downstream the dynamic thickener, the sludge sample was collected and then characterized and stored in a fridge at 4 ℃until use.

5.2.1 Analytical methods

Total solid (TS), volatile solid (VS), total chemical oxygen demand (COD), organic nitrogen ($N-N_{org}$), total phosphorous concentrations were quantified according to APHA (2012). Soluble COD (sCOD), ammonium nitrogen ($N-NH_4^+$), orthophosphate and Alkalinity concentrations were measured after filtration of the sample on 0.45 µm-membrane. pH were measured with a VWR^{TM} sympHony^{TM} meter.

5.2.2 Hydrothermal Conversion and Product Analysis

Hydrothermal conversion typically occurs between 120 and 250 ℃ under autogeneous pressure (up to 50 bar), but below the critical point (Lucian and Fiori 2017). The present work utilized a standard 50 mL stainless steel batch reactor rated to withstand 300 ℃ and 140 bar, with constant temperature and pressure monitoring, as described previously (Fiori et al. 2014). The thickened sludge were used as-received, loading the reactor with 35.0 $\pm$ 0.1 mL biomass, which maintained a biomass (dry biomass)

to water ratio of about 0.05:1. Prior to each run, the reactor was sealed and purged with nitrogen gas. It was heated to the desired reaction temperature (150 or 170 ℃) and held at the set point for the desired reaction time (30 or 60 minutes). At least three experimental runs for each of the four temperature/time combinations were performed. After the reaction time, the reactor was cooled by placing stainless steel disks on the bottom and blocking compressed air into the outer walls. The reactor was cooled to ambient in less than 15 minutes. The resulting hydrolysed sludge was characterized by measuring TS, VS, pH, COD, organic nitrogen and phosphorous. To measure NH_4^+ nitrogen, orthophosphate and soluble COD, samples were screened through a 0.45 μm filter.

5.2.3 BioMethane Potential (BMP) tests

The Biochemical Methane Potential test is a methodology used to determine the biodegradability and potential to produce methane under anaerobic conditions for organic materials. The investigated material is mixed with an anaerobic bacteria culture, namely inoculum, normally sampled from an active biogas plant, and incubated for a period of 30–60 days (Strömberg et al. 2014). For optimal performance, the mixture should be kept at a stable temperature, normally at about 37 or 52 ℃, and continuously mixed to minimise mass transfer limitations. The organic material, often called substrate, is degraded through a multistep biochemical process with the gaseous compounds methane and carbon dioxide as the major final products (Strömberg et al. 2014). In this work, the inoculum was collected from the anaerobic digester of Trento nord WWTP, Italy. The inoculum was incubated for 45 day at 35 ℃ order to consume all the residue biodegradable COD and reach endogenous condition. The BMP tests were conducted in 135 mL glass (pirex) bottles: each sample of sludge hydrothermally treated was mixed with inoculum keeping the ratio $gVS_{substrate}/gVS_{inoculum}$ lower than 0.5 in order to avoid VFAs accumulation as suggested in VDI4630 (2006). 100 mL of the mixture was than putted in the glass bottle and sealed with capping equipped with silicon membrane, leaving about 35 mL of headspace. In the end the headspace was purged with nitrogen blowed through a couple of needles (one to blow nitrogen and the other to purge air from headspace) for 5 min. Three bottle for each sample of sludge hydrothermally treated were used. Moreover, three BMP tests were performed with only inoculum in order to delete the contribution of the inoculum in the biogas production (Blank - B). In the end, three BMP test were performed with untreated sludge, in order to assess the improvement of the biogas production (Reference - rif.) The BMP tests were performed leaving the bottle in a thermostated bath at 35 ℃ for several days. To measure the biogas, Ideal

Gas Law was applied: a pressure gauge was used knowing temperature and headspace. To measure methane, instead, the biogas produce was fluxed through a column filled with a solution of $NaOH$ 2M: at high pH the CO_2 dissolves in water, so the gas measured was only methane. In the first 10 days the measurement of biogas and methane were performed almost everyday for safety reason, in the following days the measurement was carried out with decreasing frequency. To compare biogas production results, the volume of biogas measured at ambient conditions in the batch test has to be firstly converted to the volume at standard conditions using the ideal gas law 5.2.1 (VDI4630 2006):

$$V_{STP,HT} = V_{HTC} \frac{(p_{test} - p_{w,test})}{p_0} \frac{T_0}{T_{test}} \tag{5.2.1}$$

where $V_{STP,HT}$ is the standard volume of biogas from the hydrothermally treated sludge (mL), V_{HT} is the biogas volume measured in the BMP bottle (mL), p_{test} and T_{test} are, respectively, the pressure ant the temperature of the BMP bottle, $p_{w,test}$ is the water vapour pressure computed at T_{test} and, finally, p_0 and T_0 are, respectively, the standard pressure and temperature (p_0=1.01325 bar, T_0=273.15 K). Then, in order to consider BMP tests performed in different reactor types and at different loading rates, the specific volumes of biogas and methane are calculated, usually using COD, TOC or VS as the basis. The total biogas yield (Y_{biogas}, expressed in $mL\ biogas\ gCOD^{-1}_{added}$) and the methane yield (Y_{CH4}, expressed in $mL\ CH_4\ gCOD^{-1}_{added}$) are generally computed respectively by using equations 5.2.2 and 5.2.3:

$$Y_{biogas} = \frac{V_{STP,HT}}{C_0} \tag{5.2.2}$$

$$Y_{CH_4} = \frac{V_{STP,HT}}{C_0} \times \%_{CH_4} \tag{5.2.3}$$

where $V_{STP,HT}$ is the standard biogas volume (mL) produced in bottle from the hydrothermally treated sludge, C_0 is the mass of substrate added to the system, in terms of grams of COD, TOC or VS and $\%_{CH_4}$ is the volumetric fraction of methane (Erdogan et al. 2015).

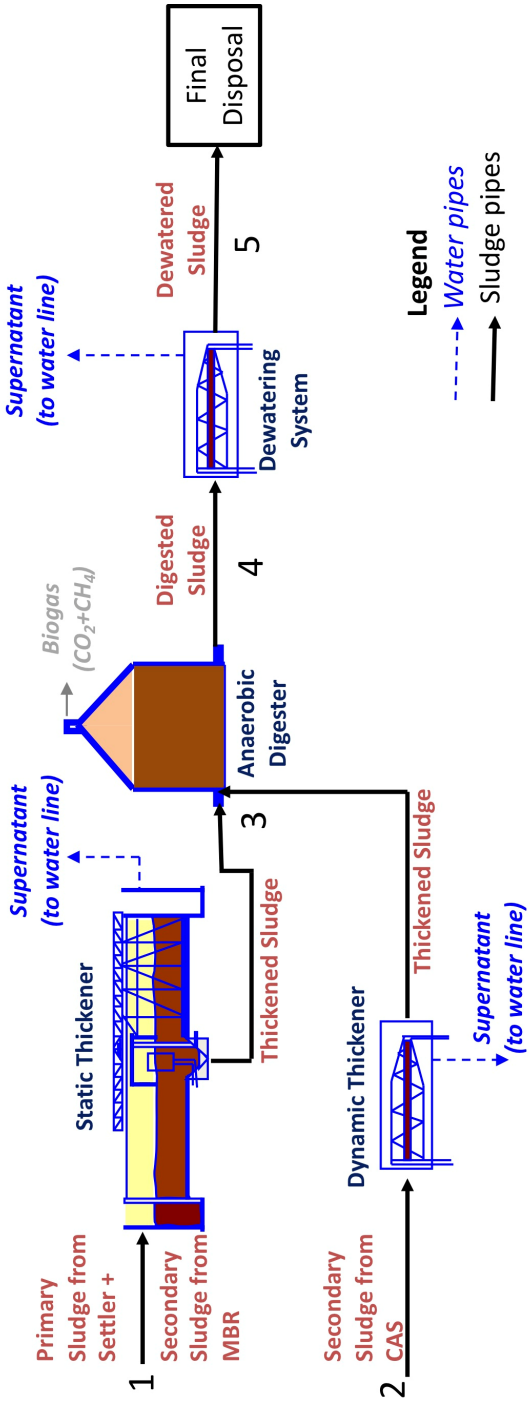

Figure 5.1: schematic of wastewater treatment plant in Trento, Italy identifying sludge samples used in the present work.

5.3 Results and discussions

Table 5.1 reports initial sludge, inoculum and treated sludge characterisation. The hydrothermal treatment, basically, solubilised organic matter increasing the soluble COD concentration, but VS and total COD weren't affected by the process.It is also possible to observe that organic nitrogen slightly decrease while ammonia nitrogen slightly increase. The main consequence generated by the hydrothermal processes is represented by the solubilization of COD due to the destruction of the cells walls. Indeed, the increase in the concentration of soluble COD can be espressed as in Eq. 5.3.1:

$$Solubilisation = \frac{SCOD_T - SCOD_0}{COD_0 - SCOD_0} \tag{5.3.1}$$

where $SCOD_T$ is the concentration of soluble COD after hydrothermal treatment, $SCOD_0$ is the initial concentration of soluble COD and COD_0 is the initial concentration of total COD. The solubilisation rate were 23, 27, 18 and 20 % for sludge treated at respectively 170 °C/30 *min*, 170 °C/60 *min*, 150 °C/30 *min* and 150 °C/60 *min*. Figures 5.2 and 5.3 report respectively the cumulated biogas production and the cumulate methane production for all the sample: it is possible to observe that the best methane production was reached with the sludge treated at 150 °C for 60 *min*. It is possible to compute the standard gas production (SGP) and the standard methane production (SMP) from the data collected during the trial, defined respectively in Eqs. 5.3.2 and 5.3.3:

$$SGP = \frac{V_{biogas\ substrate} - V_{biogas\ inoculum}}{VS_{substrate}} \tag{5.3.2}$$

$$SGP = \frac{V_{CH_4\ substrate} - V_{CH_4\ inoculum}}{VS_{substrate}} \tag{5.3.3}$$

The SGP were 338.7, 325.1, 300.9 and 354.8 $mL\ biogas\ gVS^{-1}_{added}$ for sludge treated at respectively 170 °C/30 *min*, 170 °C/60 *min*, 150 °C/30 *min* and 150 °C/60 *min*. The SMP were 205.6, 197.4, 201.6 and 228.8 $mL\ CH_4\ gVS^{-1}_{added}$ for sludge treated at respectively 170 °C/30 *min*, 170 °C/60 *min*, 150 °C/30 *min* and 150 °C/60 *min*, involving that the volumetric percentage of methane were respectively 62, 62, 69 and 66 %. Comparing these results with the reference case, the production of biogas were increased of 26, 23, 24 and 33 % respectively for sludge treated at respectively 170 °C/30 *min*, 170 °C/60 *min*, 150 °C/30 *min* and 150 °C/60 *min*. In literature the overproduction of biogas obtained by means of hydrothermal treatment is in the range of the 33-68 % (Qiao et al. 2011; Pérez-Elvira and Fdz-Polanco 2012; Pérez-Elvira et al. 2008).

Table 5.1: sludge, inoculum and treated sludge characterisation.

Analysis	**Sludge**	**Inoculum**	**170 °C 30 min**	**170 °C 60 min**	**150 °C 30 min**	**150 °C 60 min**
Total Solids [%]	4.98	5.63	4.82	5	4.67	4.61
Volatile Solids [% of TS]	3.69	3.87	3.56	3.58	3.34	3.36
Total COD $[gCOD\ L^{-1}]$	51.6	52.8	55.4	54	51.9	52.6
Soluble COD $[gCOD\ L^{-1}]$	6.8	1	17.3	18.92	14.8	15.8
Organic Nitrogen $[gN - N_{org}\ L^{-1}]$	3.24	1.85	3.9	4.08	3.44	3.29
Ammonia Nitrogen $[gN - NH_4^+\ L^{-1}]$	1.04	2.01	0.66	0.81	0.82	0.92
Total Phosphorous $[mgPL^{-1}]$	585	206	622	605	589	585
Orthophospate $[mgPL^{-1}]$	1.8	23	14	9	2	3
pH [-]	6.68	7.51	5.8	5.8	5.8	5.8
Alkalinity $[mgCaCO_3\ L^{-1}]$	-	5000	-	-	-	-

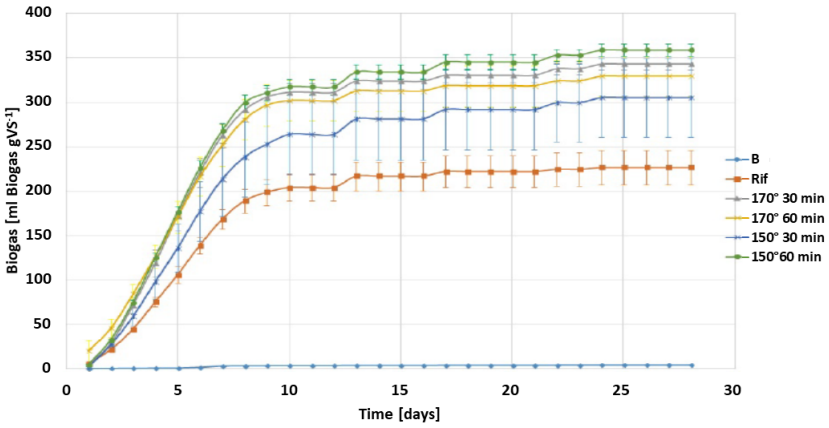

Figure 5.2: cumulated biogas for all the sample.

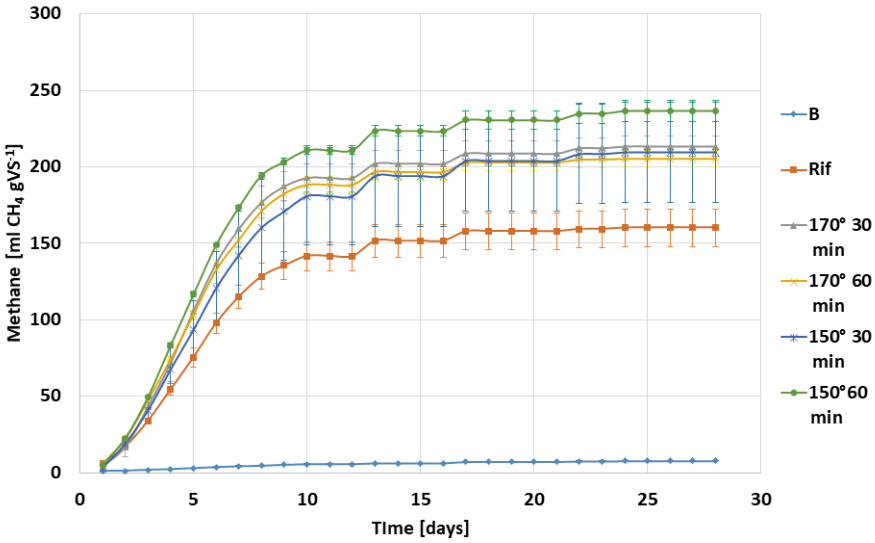

Figure 5.3: cumulated methane for all the sample.

Concerning the run at 170 ℃and 60 min, Qiao et al. (2011) found a SGP of 339.0 $mL\ biogas\ gVS^{-1}_{added}$ and a SMP of 257 $mL\ CH_4\ gVS^{-1}_{added}$, in the present work SGP and SMP in the same condition were 325.1 $mL\ biogas\ gVS^{-1}_{added}$ and 197.5 $mL\ CH_4\ gVS^{-1}_{added}$, so the biogas production are similar, while the methane production are quite different. Concerning the run at 150 ℃and 30 min, Kim et al. (2015) found a SGP of 293.0 $mL\ biogas\ gVS^{-1}_{added}$,while in the present work SGP in the same condition was 300.9 $mL\ biogas\ gVS^{-1}_{added}$, so the biogas production were similar also in this case. In Figure 5.4 the daily biogas production for

all the sample is reported. As it is possible to observe, the daily biogas production increases in the first days of the run, reaching the maximum between the fifth and the sixth day. Subsequently, the daily production decreases fastly until reaching values near 0. It is possible to compute

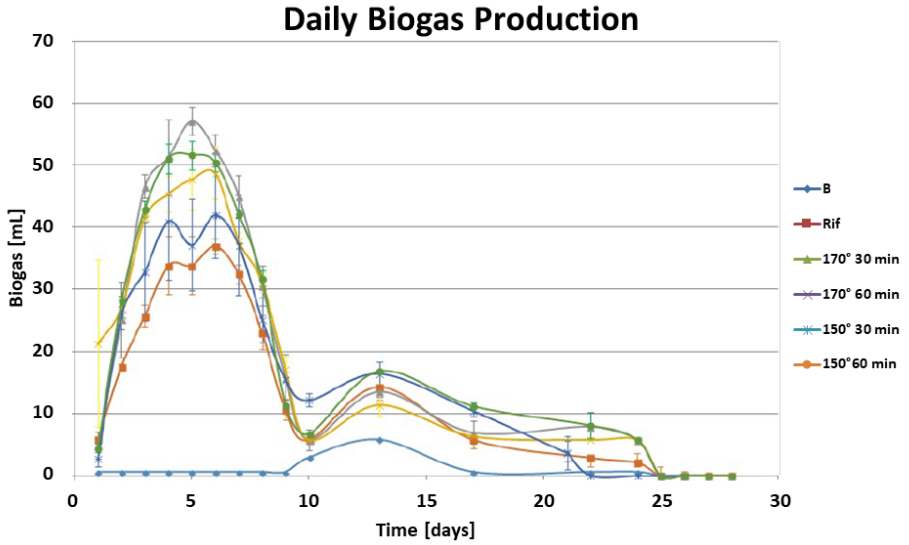

Figure 5.4: daily biogas production for all the sample.

the hydrolysis constant k_H (Eq. 5.3.4), that is fundamental due to the fact that hydrolysis is the limiting step.

$$\frac{dS}{dt} = -k_H \; S \tag{5.3.4}$$

where k_H is the hydrolysis constant (d^{-1}) and S is the concentration on the biodegradable substrate. Separating the variables it is possible to obtain Eq. 5.3.5:

$$\ln \frac{B_\infty - B}{B_\infty} = -k_H \cdot t \tag{5.3.5}$$

where B_∞ is the max biogas production, B is the production at time t, t in time and k_H is the hydrolysis constant. The value of k_H is the slope of the obtained straight line from Eq. 5.3.5. For untreated sludge and sludge treated at 170 °C/30 *min*, 170 °C/60 *min*, 150 °C/30 *min* and 150 °C/60 *min*, the k_H were 0.1501, 0.1657, 0.1684, 0.1445 and 0.1649 d^{-1} or respectively 6.66, 6.03, 5.90, 6.92 and 6.06 d if we consider the value $1/k_H$. Except for one case, all the k_H of treated sludge are higher than k_H of untreated sludge, indicating that hydrolysis step is accelerated. In the end, all the standard analysis performed on the samples were repeated at the end of BMP tests. Concerning the TS, the reference sludge removed

the 15 % of TS, while the hydrothermally treated sludge removed the 16-18 % of TS. Concerning the VS, the reference sludge removed the 18 % of VS, while the hydrothermally treated sludge removed the 20-24 % of VS. The anaerobic digestion of treated sludge removed about 50 % of the soluble COD and about 20 % of the total COD, while for the reference case the removal were 10 % and 15 % for the total and soluble COD respectively. In the end, nitrogen compounds had very high concentrations at the end of BMP test, about 2-3 $gN - NH_4^+ \ L^{-1}$ and 2-3 $gN - N_{org} \ L^{-1}$ and the pH were about $8.5 - 8.9$ leading to a possible ammonia inhibition, so for future work higher concentrations of $CaCO_3$ in order to buffer the system are required.

5.4 Conclusions

BMP tests where performed on sludge treated by means of hydrothermal conversion. The operative conditions studied were 150 ℃ and 170 ℃ at 30 and 60 minutes and the process led to an increased biogas production between 23 and 33 % compared with reference sludge. The system was tested mainly in order to successively perform BMP tests on hydrothermal carbonisation liquor at relative low temperature, namely 190 and 200 ℃ in order to avoid the formation of toxic compounds. Actually, BMP tests on HTC liquor sampled after HTC of dewatered sludge at 190 ℃and and 60 min are on going.

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Chapter 6

Conclusions

HTC of sewage sludge has great potential to become a sustainable conversion process for the management of sludge and the production of a wide variety of valuable products. For the purpose, a new HTC reactor was designed and constructed with the aim of assess the heat of reaction of HTC process; the data obtained encourage an in-depth analysis of the heat of reaction for many other biomasses and operative conditions, such as residence time, temperature, and biomass load. In this Thesis work, the HTC implementation for sludge treatment has been studied in terms of main operative parameters, products, applications and energy assessment. HTC process temperature and residence time, initial sludge composition and concentration, nutrients concentration result as the main parameters, which influence the production of hydrochar by means of HTC process. Hydrochar can be exploited in different ways, mainly as a biofuel, as a soil improver and as potential adsorbent. Especially the adsorbent application need further studies. In order to produce hydrochar and processing the HTC liquor through anaerobic digestion, the HTC temperature and treatment time should not be higher than 180 - 200 ℃ and 15 – 60 min, respectively, because higher temperatures and higher treatment time lead to the formation of not biodegradable and / or toxic compounds. For a full-scale implementation of the HTC process in a WWTP, further studies are needed in order to investigate the effect of HTC process waters on stable operations of anaerobic digestion, considering the fate of emerging contaminants and the long-term effects of recalcitrant and toxic compounds, which will be accumulated in the whole system. Moreover, nowadays hydrochar hasn't is own legislation, so, at least in Italy, it is still considered a waste: further studies are necessary in order to apply the circular economy concept and allow the conversion of hydrochar to a real valuable and exploitable product. Our research group really believes in HTC technology, so a company was founded at

the end of October 2017, namely Carborem s.r.l. As a company our team won a grant that will allow us to design and hopefully construct a pilot plant of the order of 1 or 2 thousand tons of sludge for year within 2019.

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Conventional Activated Sludge (CAS) systems have been widely implemented to treat wastewater. CAS systems produce huge amounts of waste sludge and its subsequent treatment represents up to 65 % of the operational costs of Waste Water Treatment Plants (WWTPs). The final disposal of sludge is usually performed by landfilling or incineration, involving severe environmental issues.
In order to reduce sludge amount, many studies have been conducted, developing new technologies. One of these technologies is HydroThermal Carbonisation (HTC), where sludge is heated up to 180 - 250 °C at water vapour pressure producing a solid product enriched in carbon for different possible exploitations.
The aim of this work is to apply HTC to different kinds of sludge such as thickened sludge, digested sludge and dewatered sludge and compare the behaviour of the solid and liquid phases produced by the process. For the purpose, a new HTC reactor was designed in accordance with standard technical requirements for vessel under internal pressure and experimental tests were performed at different operating conditions in a lab batch reactor capable to withstand high pressure (140 bar) and temperature (300 °C). In order to compare the HTC products of the different kinds of sludge, the hydrochars from HTC at different operative conditions were characterized in order to explore possible application of hydrochar and HTC process water.

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